

Some Isotope Aspects of a Hydrogen Energy Concept

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Abstract - A concept of energy cycling through hydrogen is considered taking into account the isotope (D/H) aspect. It is based on a two-step cycle: 1.- Storing of electrical energy into hydrogen *via* water electrolysis and 2.- Bringing a part of the stored energy back to the system at the moment of demand *via* the fuel cell plant. Both steps have an impact on the isotope compositions of working fluids at the point of transfer, due to isotope effects appearing. These effects are characterized by the D/H isotope separation factor. The model considers possibilities to improve the cycle efficiency by simultaneous improvement of energy and isotope separation efficiencies of both steps. For the first time the role of hydrogen fuel cells in a deuterium/hydrogen isotope separation process was considered.

Keywords: Hydrogen energy, Water electrolysis, Fuel cell, Deuterium, Isotope separation

1. Introduction

Hydrogen is the key energy medium for the „hydrogen-based economy” of the future, due to its unique properties, i.e., production for storage, gas-line or truck transport, and transfer back to energy on demand at the place of usage.

There are three hydrogen isotopes: light hydrogen or protium (H), heavy hydrogen or deuterium (D), and super-heavy hydrogen or tritium (T). The heavy hydrogen isotopes are of great importance in the nuclear energy technology, although nuclear energy is not a dominant energy source at present time. Its world share is about 7.5 %, but it will probably rise faster than that of other types of energy in the near future. Deuterium in the form of heavy water (D₂O) is used in natural uranium fuelled fission reactors, both as the neutron moderator and as coolant. A heavy water nuclear power reactor needs roughly one tonne of D₂O per megawatt (electric) installed [1,2]. The average abundance of deuterium in natural hydrogen all over the world is about 150 ppm (*parts per million*). Main raw material for its production is water.

Both D and T are promising fuel components for the thermonuclear fusion reactors in the future.

Briefly, we can say that the importance of hydrogen, along with its isotopes, will rapidly rise in the coming decades toward the concept of hydrogen economy [3].

The idea of this work is to base a hydrogen energy concept on an open energy cycle that includes: (i) the

alkaline water electrolysis (AE) to produce hydrogen for storing electrical energy, and (ii) its transfer back to electrical energy at the moment of demand in a fuel cell power plant (FCPP). Process (i) delivers deuterium depleted hydrogen gas (along with oxygen) on one side, and deuterium enriched water remaining in the alkaline electrolyte, relative to the feed content, on the other, while process (ii) consumes hydrogen and oxygen evolved in step (i), giving electrical energy and the deuterium enriched water relative to the burning hydrogen. In this way both AE and FC play the role of *isotope separating units*¹. In both cases isotope separation is carried out with a help of the so-called isotope separating agent. This agent divides the feed stream into two outgoing streams, the heads one (by convention it is assumed to be enriched in the desired isotope - the desired isotope here is deuterium), and the tails one (depleted). The idea of the fuel cell (FC), not considered before in such a context, was introduced into this rather old *hydrogen production—*isotope separation concept, to improve the overall energy cycling efficiency. Dependence of that efficiency on the energy efficiency of AE and FC in particular, as well as on the isotope separation efficiency of both devices, expressed through some fundamental process parameters, is discussed with an intention to point to some relevant facts rather than to make a precise calculation, although some basic relations would be developed.

An approach which also considers a combination of electrolyzers and fuel cells, but with a focus on ‘a novel deuterium separation system’ and without taking isotope separation efficiency of FC into account, was recently discussed [4].

¹ A fundamental measure of the separation efficiency of a specified separating unit (or stage) is the *stage separation factor*, α , or simply the *separation factor*. This factor is defined by the following equation:

$$\alpha = \frac{x'}{1-x'} : \frac{x''}{1-x''} \quad (1)$$

where x' and x'' are atom fractions of D (desired isotope) in the *heads stream* (enriched) and the *tails stream* (depleted), while $(1 - x')$ and $(1 - x'')$ are corresponding fractions of H, respectively. For details see Fig. 1.

Electrolyzers and fuel cells are simple, efficient, clean and silent electrochemical devices, with no moving parts. The only effluents of FC are pure water, electrical energy and heat.

1. Description of the concept

The idea of the concept is schematically represented in Fig. 1. The general scheme includes:

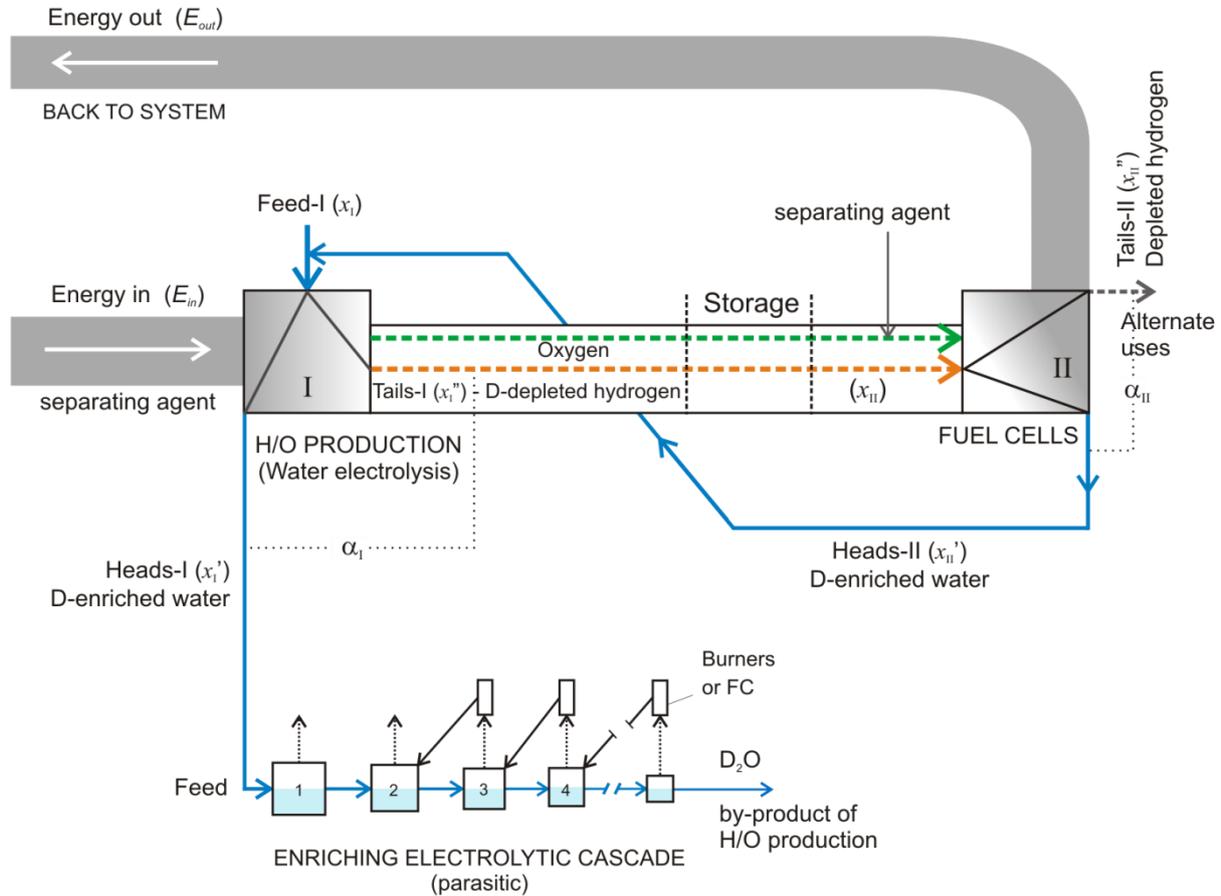


Figure 1: Schematic representation of an open energy-hydrogen-energy storage cycle: Reversible power plant concept with a parasitic D/H isotope enriching cascade. I – Energy-to-hydrogen transferring/separating unit; II – Hydrogen-to-energy transferring/separating unit; x represents the atom fraction of the desired isotope (D) in corresponding streams.

(i) Transfer of electrical energy into hydrogen in the Device I for storing, via the water electrolysis from alkaline electrolytes. This device is continuously fed with pure water. In the sense of energy terms, this is the *energy transferring* device. This step is directly characterized by the energy consumption per mass unit of hydrogen evolved, which actually means the *current density/cell voltage* characteristics of the electrolyzer under certain conditions. They can be easily measured. We did that on a laboratory scale for some electrode materials, either in the pure KOH electrolyte or in combination with some activators added *in situ* to that electrolyte to improve catalytic properties of electrodes [5]. At the same time this device is the *isotope separating* unit, where energy plays the role of the isotope separating agent. It is supposed to be an *electrolyzer with a constant level* [6]. In such a unit the

deuterium concentration in both outgoing phases proportionally rises during electrolysis until so-called boundary enrichment, remaining the ratio determined by the separation factor (Eqn 1). The heads stream is water remaining in the electrolyte, while the tails stream is evolved hydrogen.

Device I is a single separating unit or stage, to which an enriching cascade can be attached as a bypass, to further process the enriched stream until needed concentration of deuterium is attained. In principal, very small part of the material processed goes to that cascade [7].

(ii) Bringing a part of the entire energy in the form of electricity back to the system via the fuel cell based power plant (Device II). In this device, hydrogen (in the presence of oxygen or air) is consumed to be transferred back to electrical energy. In this way,

deuterium from the feed material is stripped twice. Consequently, oxygen added to enable this transfer is the *isotope separating agent* of this *energy transferring* device. In terms of isotope separation, this device can also be considered as a *single unit* or *stage*, delivering water (heads stream) enriched in D relative to the incoming hydrogen gas. Due to that, the water leaving the unit II is expected to be above the natural level, which mostly depends on processes in FC. Even if there is no difference in isotope contents between this water and the feed one, the least benefit for the cycle can be found in returning it back to the device I to be used for feed, because the FC product-water is clean and needs no pre-treatment. Conclusively, water partly serves here as the working fluid. A bigger part of it moves between units I and II, while another part, taken from the electrolyzer of the unit I to feed the enriching cascade, is further processed. Of course, that part should be continuously supplemented from feed.

The hydrogen energy-storing system proposed in this work is actually the reversible power plant concept in which hydrogen serves as the energy carrier. It assumes, by definition, storing of low-cost off-peak electrical energy, combined with simultaneous D/H isotope enrichment. The energy stored in this way can be transferred back to electricity to be used at times of high demand at a much higher price. An analogous scheme was discussed more than a decade ago [8], but with no analysis of the isotope separation possibilities.

2. Discussion

It is clear that the cycle illustrated in Fig. 1 has a negative energy balance, the degree of which is actually the net energy cost of cycling, $\Delta E = (E_{in} - E_{out})$. It substantially depends on the transferring efficiencies at the units, f_I and f_{II} , given as

$$f_I = \frac{m_{H_2}}{E_{in}} \text{ and } f_{II} = \frac{E_{out}}{m_{H_2}}, \text{ i.e. } \frac{E_{in}}{E_{out}} = \frac{1}{f_I \cdot f_{II}} \quad (2)$$

Here m_{H_2} is the total amount of hydrogen produced per cycle (mol) consuming the input energy E_{in} (at a low off-peak price C_{el-in} ; € J^{-1}), the output energy equivalent of which is E_{out} (to be sold at a peak price C_{el-out} ; € J^{-1}).

Since we do cycling for the purpose of storing energy, the ΔE value predominantly contributes to the total cost of the cycling (storing). That cost also includes the storage cost in particular, for the given amount of hydrogen, as well as the cost of transport (if any). In addition to that, the synergy between production of hydrogen and the heavy water 'by-production' offers an extra impact on the final price. In fact, the total cost of energy storage should be reduced for benefits derived from the isotope enrichment. Thus, the total cost of the cycle (€) is given as

$$c = E_{in} C_{el-in} - E_{out} C_{el-out} + c_{sto} + c_{tr} - c_{ise} \quad (3)$$

where

$$c_{sto} = C_{sto} \cdot m_{H_2} = C_{sto} \cdot \frac{E_{out}}{f_{II}} \quad (4)$$

is the cost (€) that should be paid to store the total amount of hydrogen (m_{H_2} , mol). Here C_{sto} is the corresponding price of hydrogen storage (€ mol^{-1}).

Similarly,

$$c_{tr} = C_{tr} \cdot m_{H_2} = C_{tr} \cdot \frac{E_{out}}{f_{II}} \quad (5)$$

where C_{tr} is the price of transport of that amount of hydrogen (€ mol^{-1}).

In principal, benefits expected from the isotope enrichment per one cycle, c_{ise} (€), can be estimated by taking into account the total amount of deuterium in the leaving hydrogen. It is a useful, but not the only measure of the 'isotope benefit' of an optimized cycle. Now, we can write

$$c_{ise} = C_{ise} \cdot x_{II} \cdot m_{H_2}, \quad \left(x_{II} = x_I = \frac{m_D}{m_{H_2}} \right) \quad (6)$$

where m_D (mol) is the total amount of pure deuterium in evolved gas, while C_{ise} is its unit price ($\text{€ mol}^{-1} D$)². Actually, this price accounts for all isotope contributions to the total cost reduction at a given average deuterium content in the system. Its precise estimation, although possible, is not an easy work at all.

Other relevant deuterium contents, like that in the electrolyte of unit I, or that in the product water of unit II, can also be considered in such a context, because they are all inter-related. At the same time, they are all dependant on the values of D/H isotope separation factors, see Fig. 1. We measured these factors experimentally on lab scale units and found them to be very high (up to 10) [9]. As far as we know such measurements on FC were never made before.

Finally, after introducing equations (2, 4, 5 and 6) to the equation (3), and division by the output energy, E_{out} , to obtain the unit price of cycling, C (€ J^{-1}), we now have

$$C = \frac{1}{f_I \cdot f_{II}} C_{el-in} - C_{el-out} + \frac{1}{f_{II}} (C_{sto} + C_{tr} - C_{ise} x_{II}) \quad (7)$$

In the first place, this price depends on the ratio of the input and output energy in the cycle. According to the equation (2), it is inversely proportional to the $f_I \cdot f_{II}$

² By the way, price of heavy water varies from about 400 \$/kg D₂O to about 600 \$/kg D₂O. These data can be found in some publications [1,10] or on the Internet.

product, thus, the higher the transferring efficiencies of the units I and II, the lower the E_{in}/E_{out} ratio and lower C . These efficiencies essentially depend on the nature or processes taking place in units, as well as on the conditions a specific process is run under. One of these efficiencies has an additional impact on the final price through the second part of the equation (7).

Under input and output energy we understand electrical energy, the market price of which is expressed as C_{el-in} and C_{el-out} , respectively. These prices can be either lower or higher than the production one, depending on the market supply and demand at a moment. Together with the price of storage and transport they contribute to the final price. However, the storage and transport prices were not subjected to this analysis.

3. Conclusions

The unit price of energy cycling (C) is a function of the following crucial parameters:

- The input-to-output energy ratio (E_{in}/E_{out}), which directly depends on the transferring efficiencies f_i and f_{ij} . The latter ones can essentially be improved by using advanced materials and design.
- Prices of electrical energy. For hydrogen production and simultaneous deuterium enrichment, electrical energy should be as cheap as possible. On the other hand, we estimated that the *output* energy should be at least twice more expensive than the *input* one, since it is generated and sold at times of highest demand. Accompanied with efficient simultaneous D/H isotope enrichment it makes such a cycle quite attractive.
- The average content of deuterium in the system, expressed through x_{II} . This parameter is strongly dependent on the separation factors on AE and FC.

Almost the only disadvantage of electrolyzers is the expensive energy they consume. However, fuel cells still have significant disadvantages at present time. They are expensive, since there is no large scale production. Consequently, high power stations (hundreds of megawatts) are not yet industrially developed.

The power plant system described here is a reversible one. It absorbs the excess load at times of high output and low demand, contributing at the same time to the relaxation of the system. The heavy water plant is a parasitic one. Its production cost is mainly based on using enriched water from the cycle.

Because of very low natural content of deuterium, it is necessary to process very big amounts of raw material for a reasonable quantity of heavy water produced. Therefore the above isotope concept is more appropriate for big systems, transferring huge amounts of energy to hydrogen.

High D/H isotope separation factors obtained experimentally have pointed out the need to consider the hydrogen energy concept discussed in this work quite seriously.

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