H_2: energy vector or source?

The di-hydrogen presents obvious advantages: as a fuel it can burn without emitting greenhouse gases or particles and as a means of storing electricity, it enables large scale and long period storage. In comparison with other methods of storage, gas storage mainly underground, allows for months of autonomy in a country such as France when all our batteries will be empty in few minutes and our dams in few days. For many analysists, hydrogen produced from renewable electricity is the missing element which could facilitate the integration of high levels of variable renewable energy into the energy system.

At the moment, H_2 is mainly used in industry as a raw material and is only starting to be used as a fuel for cars, trains and buses. It is also essentially manufactured from methane by CO_2 emitting processes. Alternatives exist such as electrolysis that splits water into hydrogen and oxygen. When the electricity is decarbonized, this H_2 is called green H_2. If the objective is the storage of the intermittent renewable electricity, fuel cells then allow to go back to electricity. Today these processes are not yet very efficient. Power to gas to power results in a 70% loss of energy, but improvements are expected, especially with the reversible Solid Oxide high temperature Fuel Cell (SOFC). Bacteria activity, algae and oxidation processes of for instance iron rich material are also potential sources of H_2 [1]. All these methods are not at the same stage of development (technology readiness levels TRL vary from 1 to 8) and do not result in a homogeneous H_2 price. Trying to predict which process will be the cheapest in a few years and thus predict "the" winner is what a lot of consultant and strategy departments are working on but this may not be the best approach. The most important trend in the new energy world is decentralization. Depending on the local constraints, the optimum role of H_2 in a green energy mix will differ and therefore the best technology will depend on the use for and the users. In addition, the transport of H_2 over large distances by boat is not easy; economically it is close to being a killing factor – the opposite of methane which can easily be liquefied. Liquefaction of H_2 consumes up to half of its energy.

Today industry is mainly focusing its efforts concerning green H_2 on reducing the price of electrolysis and fuel cells. This means that many companies are considering H_2 as a vector. However, two game changers are emerging which could be very disruptive.

First: native H_2

Natural H_2 produced by the water/rock interaction has been observed for long time but it was assumed that this production mainly occurred on a large scale along the mid oceanic ridges where hot oceanic newly created crust is in contact with sea water [2]. Roughly this reaction is an oxidation reaction of the Fe^{2+} (or Mg^{2+}) and H_2 is released. The estimation of this production is between 4 000 and 10 000t/year/km of ridge.

New Caledonia: the hydrogen released from the subsurface reacts with the CO_2 in the atmosphere resulting in the carbonate precipitation. A natural carbon capture, utilization and storage (CCUS) process!

The conditions of deep water in the middle of nowhere with very hot fluids seem to exclude any economically viable production. However, for the past ten years, new data has shown that similar reactions happen at lower temperatures such as in Oman or New Caledonia [3] (*figure*) and that another oxidation reaction that takes place in old cratons where iron rich rocks are present also results in the continuous production of H_2 (in Russia [4], in the USA [5] and in Brazil [6]). At the same time, an accumulation of H_2 has been unexpectedly found in Mali at a shallow depth (110 m); the people who drilled the well were looking for water but the H_2 that they found instead has now been in production for five years [7]. It is burned to produce electricity for the town. The pressure hasn't decreased during all these years strongly suggesting a continuous generation of H_2. This discovery also proved that carrier bed and seal exist for H_2 as for any other fluids in the subsurface. In 2018, the permanent monitoring of H_2 emanations carried out in Brazil by Engie has confirmed the continuous emission of H_2 in the studied area although the rate is not constant and varies during the day. The possibility of producing large and cheap quantities of H_2 from the subsurface is now a realistic hypothesis and various groups are working to better define the geological conditions that will allow long term production.

Second: H_2 produced using plasma torching

The second game changer comes simultaneously from the two main natural gas producers: the USA and Russia. H_2 could be produced using plasma torching of methane with black carbon as a by-product which, at least as a first step, could allow the process to be economically viable. The first large scale installation is currently managed in the States by monolith [8] and Gazprom announced by mid-2018 *via* a press release that they will massively invest in that technology in order to provide H_2 to western Europe in the coming decades with 100% H_2 in 2050... [9]. In Russia, as in the USA, because they will use up their huge reserves of cheap natural gas and their already in-place infrastructures, as soon as the plasma torch becomes cheaper, this H_2 is expected to rapidly reach a very competitive price. The current reserves of gas – 200 years of consumption worldwide – ensure the durability of such a green H_2 resource (from CH_4 but without producing CO_2). The technology used by Monolith is for a part tested in France, with Laurent Fulcheri's group at the Centre for Processes, Renewable Energies and Energy Systems at Mines ParisTech PSL Research University.

In another words, the probability of having access in the near future to a non-carbonated "natural" gas is not zero. In which case, the need to pass via electricity to decarbonize the energy mix will be questionable. It may even turn out to be the wrong solution, and consequently the need for huge batteries to store this electricity will also be questionable.

The future is not always predictable, even when we write it, and the race for cheap, green H_2 has started. Personally, I'm not sure that the electrolysers will be the (only?) winner.

[1] Oey M., Sawyer A.L., Ross I.L., Hankamer B., Challenges and opportunities for hydrogen production from microalgae, *Plant Biotechnol. J.*, **2016**, *14*, p. 1487, doi: 10.1111/pbi.12516.
[2] Charlou J.L., Donval J.P., Fouquet Y., Jean-Baptiste P., Holm N., Geochemistry of high H_2 and CH_4 vent fluids issuing from ultramafic rocks at the Rainbow hydrothermal field (36°14'N, MAR), *Chem. Geol.*, **2002**, *191*, p. 345, doi: 10.1016/S0009-2541(02)00134-1.
[3] Deville E., Prinzhofer A., The origin of N_2-H_2-CH_4-rich natural gas seepages in ophiolitic context: a major and noble gases study of fluid seepages in New Caledonia, *Chem. Geol.*, **2016**, *440*, p. 139, doi: 10.1016/j.chemgeo.2016.06.011.
[4] Larin N., Zgonnik V., Rodina S., Deville E., Prinzhofer A., Larin V.N., Natural molecular hydrogen seepage associated with surficial, rounded depressions on the European craton in Russia, *Nat. Resour. Res.*, **2014**, *24*, p. 363, doi: 10.1007/s11053-014-9257-5.
[5] Guélard J., Beaumont V., Rouchon V., Guyot F., Pillot D., Jézéquel D., Ader M., Newell K.D., Deville E., Natural H_2 in Kansas: deep or shallow origin?, *Geochem. Geophys. Geosyst.*, **2017**, *18*, p. 1841, doi: 10.1002/2016GC006544.
[6] Prinzhofer, A., Moretti I., Françolin J, Pacheco C., D'Agostino A., Werly J., Rupin F., Natural hydrogen continuous emission from sedimentary basins: the example of a Brazilian H_2-emitting structure, *Int. J. Hydrog. Energy*, **2019**, *44*, p. 5675, doi: 10.1016/j.ijhydene.2019.01.119.
[7] Prinzhofer A., Cissé C.S.T., Diallo A.B., Discovery of a large accumulation of natural hydrogen in Bourakebougou (Mali), *Int. J. Hydrog. Energy*, **2018**, *43*, p. 19315, doi: 10.1016/j.ijhydene.2018.08.193.
[8] https://monolithmaterials.com/olive-creek
[9] www.bloomberg.com/news/articles/2018-11-08/russia-looks-to-hydrogen-as-way-to-make-gas-greener-for-europe

Dr Isabelle MORETTI,
E2S UPPA, formal Chief Scientific Officer & Top Expert at Engie, member of French Technology Academy.

*isabelle.moretti@engie.com