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From Nuclear Waste to Hydrogen Production: From Past Consequences to Future Prospect

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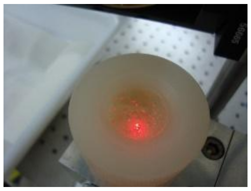
GRAPHICAL ABSTRACT:



H_2 bubbles produced by the effect of radioactivity onto water (credit: Guillaume Blain in ARRONAX, 2016)

ABSTRACT:

Nuclear wastes may not be considered as unusable materials in the sense that they deliver a free source of energy under the form of ionizing radiations that can be used to produce hydrogen (H_2) through water radiolysis. The current paradigm that define these nuclear wastes as troublesome by-products which no one uses nowadays must be shifted into a new opportunity for pure H_2 production with no CO_2 emission. Here, we propose a low-tech method to boost H_2 production by water radiolysis thanks to the catalytic effect of a suspension of TiO_2 nano-particles. We also

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demonstrate the relevance of this concept by scaling up our laboratory results. From our calculations, this radiocatalytic process can supply until 60% of the actual global demand in hydrogen (42.9 $MtH_2.y^{-1}$) and open the door, together with the green and white hydrogen productions, to the "Hydrogen century".

KEYWORDS: Nuclear Waste, Hydrogen Production, Radiocatalysis, TiO_2, LowTech Process

1. Introduction

To meet the net zero emission scenario of the International Energy Agency, about 300 Mt of hydrogen-based energy has to be produced worldwide by 2050. Currently, water electrolysis using renewable [1; 2] and nuclear electricity [3; 4] is the main industrial process envisioned to produce large amount of hydrogen with low carbon emissions. However, beyond electricity itself, many valuable resources like metals and land space will be consumed by this technology scenario. Until now, water radiolysis, as a serious alternative to produced massive amount of H_2, has been ignored. This radiolytic process of hydrogen generation is known for a century [5; 6], but the nuclear energy industry still prefers to envision the use of its electricity (from the so-called warm generator) to produced indirectly H_2 [3; 4], than taking advantage of the radiation delivered by the spent fuel. Water radiolysis occurring naturally in the Earth's crust is known to be a significant source of H_2 and to support deep microbial ecosystems [6; 7]. So much efforts have been made to manage nuclear wastes that one has forgotten that they offer a free source of radiations available all around the world. There is 390.000 tons of spent fuel worldwide awaiting their final storage facilities (Data for 2017 [8]), and many more to come in a near future as nuclear electricity is seen as good mean to mitigate CO_2 emissions.

2. Material and Methods

Four sets of samples are irradiated under Ar atmosphere to avoid the dioxygen effect: UltraPure water (UP), UltraPure water and ZrO_2 (UP+ZrO_2), UltraPure water and TiO_2 anatase (UP+TiO_2anat), UltraPure water and TiO_2 rutile (UP+TiO_2rutile). Ultrapure water resistivity was measured at 18 MΩ.cm. All solid samples were purchased from Sigma-Aldrich (99.9% Purity) and added to the solution with a ratio of 12.5 $g.L^{-1}$. The solution density is calculated at 1.052 $g.cm^{-3}$.

2.1 Irradiation source

γ-Ray irradiations experiments were performed at the ARRONAX cyclotron (Nantes – France) facility. The irradiation cells were made of PEEK (polyether ether ketone), mounted with a rotulex 19/9 glass tube and had an internal volume of 42 mL. The irradiation time range is between 1 to 60 days. γ-Ray irradiation was performed with a GSM D1 (Gamma-Service Medical®) irradiator containing a 123 TBq ^{137}Cs source. This radionuclide disintegrates in ^{137}Ba, which delivers 661.7 keV γ-Ray. A dose cartography has been performed by Fricke dosimetry [9] inside the γ-Ray chamber. The average deposited dose rate inside the aqueous samples is 420 $Gy.h^{-1}$. Such a modest dose rate has to be compared to the 28 $kGy.h^{-1}$ delivered by high activity long life spent fuel. As γ-Ray is a penetrating radiation, the dose is displayed almost equally everywhere inside the sample.

2.2 Gas Measurements

Hydrogen (H_2) has been monitored by micro gas-chromatography (µGC) using a 490-GC (VARIAN®) micro gas-chromatograph. A 5 Å molecular sieve column dedicated to H_2 separation was used, coupled to a TCD detector. The injection system and the column were purged with argon beforehand. All our chromatographic measurement were repeated 3 times, with a precision of 3 % at the 95 % confidence level.

2.3 Radiolytic yield calculation (G-value)

The G-value is defined as the number of species formed or consumed per unit of deposited energy. It is the main parameter used to express the production of one chemical species via the radiolysis mechanism. It is expressed in the international system by mol.J^{-1} and is calculated at a time t after transition of the ionizing irradiation according to:

$$G(X) = \frac{X_t}{\rho \, D} \qquad (1)$$

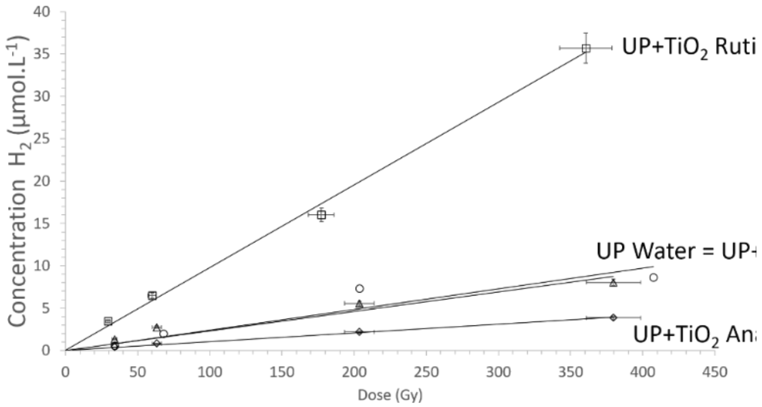
where X_t is the concentration of the species X at the time t (mol.L^{-1}), ρ is the density of the irradiated solution (kg.L^{-1}) and D the absorbed dose (in Gy; 1 Gy = 1 J.kg^{-1} of water).

Results

Liquid water is exposed to a γ source (Cs^{137}) in order to mimic the γ-ray from the radioactive waste. Hydrogen production is precisely measured for each irradiation time and applied dose rate. Titanium dioxide rutile or anatase phase powders, chosen for its photocatalytic effect [10-18], are added to the solution. Tetravalent oxide (zirconium) is also tested to underline the specific surface properties of TiO_2 with respect to H_2 generation [16; 17; 19-23].

Figure 1 presents the evolution of the radiolytic production of H_2 as a function of the applied dose, which is itself a function of time as the dose rate of the γ-source is constant. From these results one can easily observe that rutile-bearing experiment produced 4 times more H_2 than all the other ones whether they contain only water, or another polytype of TiO_2 or ZrO_2. To our knowledge, this is the highest H_2 yield measured so far in pure water solution.

This enhanced production of H_2 is specific to the TiO_2 rutile which confirms its radiocatalytic properties. Interestingly, a parallel can be made with its photocatalytic properties. Indeed, it is well described in the literature [10; 15; 18] that in the presence of UV-Visible solar radiation the TiO_2 surface in contact with water solution promote the formation of H°, OH°, $O_2^{\circ -}$ and HO_2° radicals, i.e. the same species involved in the water radiolysis mechanisms [6]. Moreover, in photocatalytic experiment, TiO_2 rutile was already identified as a scavenger of the OH° radical to enhance H_2 production on the contrary to ZrO_2 [17].



Irradiated medium	Yields G_{H2} (µmol J^{-1})
UP + TiO_2rut	0.098
UP Water	0.026
UP + ZrO_2	0.023
UP + TiO_2anat	0.010

Figure 1. Hydrogen production vs. dose, i.e. vs. the contact time between solution and γ -ray

The **Equation (1)**, (SI) is established with specific parameters which must be taken into account for an industrial H_2 radiolytic production as follow:

$$m_{H2} = G_{H2} \times \rho\, D_R \times T \times V_{sol} \times M \qquad (2)$$

where m_{H2} is the dihydrogen production (in g), ρ is the density of the irradiated solution (1.05 kg.L^{-1}, in the case of the TiO_2 rutile suspension), D the absorbed dose (in Gy, corresponding to the product of Dose Rate D_R of the γ -source in Gy.h^{-1} and the contact time t in h), V_{sol} the irradiated volume of the solution (in L), G_{H2} is the H_2 radiolytic yield (mol.J^{-1}) and M the molar weight of H_2 (2.016 g.mol^{-1}).

From the G-value determined for the TiO_2 rutile system (0.1 µmol.J^{-1}) and **Equation (1)**, one can upscale the H_2 production derived from our experiment lab conditions to realistic industrial process. Here, we envision to circulate an aqueous suspension of TiO_2 rutile around a vitrified high-level radioactive waste (Figure 2A). The water circulation circuits is connected to a degasser in order to retrieve H_2 produced by water radiolysis. The HL Radwaste size is considered as 135x44 cm with a mass of 500 kg and a dose rate D_R = 14 kGy.h^{-1}. These results are calculated for two options with a different thickness of the water layer around the waste: either 2 cm (V_{sol} = 46 L), either 10 cm (V_{sol} = 294 L) which corresponds to the average penetration depth of the Cs γ-radiation.

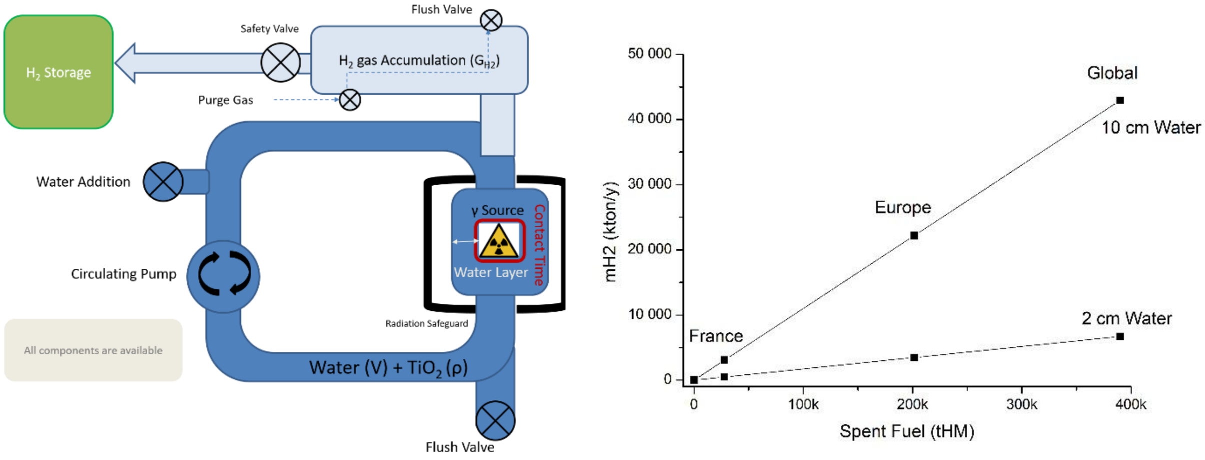


Figure 2. *A* : Scheme of H_2 production unit where the high level nuclear waste is surrounded by a water container connected to a recirculation circuit and a degaser to recover H_2. The thickness of the water layer surrounding the waste package should be around 2 to 10 cm to maximize the effect of the γ-radiation penetration. *B* : Total H_2 radiolytic production via nuclear waste inventory vs data sheet from AIEA [8] (Data inventory at 31th December 2016) with 10 and 2 cm for the water layer thickness around the waste.

The following important comments can be made from this calculation (see Eq. 2):

- G_{H2} : From our lab results we have used the 0.1 µmol.J^{-1} value, but many yield improvement can be proposed by scavenging processes which, for example, consumes hydroxyl radical and enhances the H_2 production [24; 25].
- ρ : The density of pure water is 1 kg.L^{-1}, but one must take into account the density of the aqueous suspension of TiO_2 rutile (1.05 kg.L^{-1}). This TiO_2 quantity could be optimized to enhance the yield of H_2 production.
- γ Source: In our experimental lab we have used a classical ^{137}Cs source (Dose Rate = 420 Gy.h^{-1}) which is the main γ source emitting in the spent fuel for the first part of radioactive decay (30 years). That is the reason why, from an industrial point of view, the more efficient radioactive source is the High Activity-Long Life spent fuel actually storage in different power plant (390 ktons) with an average dose rate calculated from literature data [26] to 28 kGy.h^{-1} per ton. So we can extend the actual experiment to the spent fuel due to the same source term (^{137}Cs) in both cases with a difference between the dose rate (28 vs. 0.420 kGy.h^{-1}).
- Contact Time: This time is the duration when the volume of solution is under the effect of the irradiation. In this study, we have performed experiments lasting up to 2 months and confirmed that the H_2 production occurs continuously with the TiO_2 surface scavenging the OH° species without poisoning [17]. Such a phenomenon does not happen with ultrapure water only as the Allen chain stops the H_2 production process [6]. Thus, we have chosen to calculate the H_2 production over one year to compare with other industrial processes.

- Molar Weight: We have expressed the H_2 production in term of mass to compare with other H_2 production methods already used.
- Volume of the solution (V): It is the key point for the H_2 radiolytic production. The H_2O concentration (55.5 $mol.L^{-1}$) exposed to the radiation kinetically forces the H_2 production. That is the reason why higher is the irradiated volume, higher is the H_2 production. The H_2 radiolytic production kinetic occurs at µs scale [6]. Therefore, for both cases (2 and 10 cm water layer corresponding to the average penetration depth of γ-ray), we have calculated the water flow rate accounting for the waste package geometry (46 and 294 $L.s^{-1}$, respectively).
- Production of H_2: For the 2 and 10 cm water layer, the production of radiolytic H_2 is respectively 6.7 and 42.9 MtH_2 per year if we used the totality of spent fuel actually stored in the world (value in 2017). This H_2 production can further be enhanced, as underlined in previous occurrences, by optimizing the irradiated solution volume, G_{H2}-value, TiO_2/water ratio and water composition.

3. Discussion: Consequences for low-carbon Hydrogen production

From the hydrogen industry side, the global quantity of pure H_2 calculated in **Figure 2** (6.7 and 42.9 $MtH_2.y^{-1}$) represents about 10 and 60 % of the actual global H_2 production (70 $MtH_2.y^{-1}$, with only 0.6 $MtH_2.y^{-1}$ being supplied as “green hydrogen” from renewable energy sources in 2019 [2]). Moreover, the so-called “green hydrogen” need high quantity of low-carbon electricity, metals such as Cu, Co, Ni or Li and pure water to be relevant. In the radiolytic production, the system proposed here can be considered as “low tech” due to : (i) a very modest electricity need (just to circulate solution and not to initiate electrolysis), (ii) only Titanium required as metal oxide native form and it is considered as the ninth more abundant element in the earth’s crust [27], (iii) many kind of water can be used (wastewater, seawater for example) and (iv) all materials needed are commercially available without rare or strategic metals being involved. Nevertheless, research and development on irradiated solution volume, G_{H2}-value, TiO_2/water ratio and water composition remains to be carried out to enhance the global production H_2 yield of the radiolytic process.

4. Conclusion and Perspectives

In this work, a new paradigm is proposed: spent nuclear fuel may not be seen as useless waste but as a new unused free-carbon energy source via the H_2 radiolytic production by a lowtech process. This system displays many advantages in addition to the classical “green hydrogen” ones:

- The nuclear production energy is a decarbonized one, so the wastes produced via this technology too.
- The long-live radioactivity delivered by nuclear waste allows to use it for many centuries (> 300 years) with a low technology process.
- All spent nuclear fuel wastes produced from the start of the nuclear industry in 50’s can be used by this process (in 2017, 390 ktons).
- By the revival of the nuclear industry in the world (at least two-fold more in 2050), more and more unused nuclear wastes will be available for this H_2 production process.
- At the contrary to the “green hydrogen” process which proposes to convert electricity in hydrogen, which could be used for other decarbonized sectors, and reconvert it to

electricity with loss of yield; the radiolytic process proposes to convert unused nuclear waste in electricity via the hydrogen production.

- Calculations from our experiments yield an H_2 production ranging give between 6.7 and 42.9 $MtH_2.y^{-1}$, depending on the water layer thickness considered around the waste. Its represents between 10 to 60 % of the global demand in hydrogen and at least 10-fold the present day actual production of “green hydrogen”.

However, many parameters remain to be optimized to improve the H_2 production yield. These parameters are as follow: irradiated solution volume, initial G_{H2}-value, TiO_2/water ratio and water composition in order to accommodate the results presented here to the industrial realities.

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