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1 “Impact of γ -radiation on carbon steel anaerobic corrosion and H₂
2 production.”

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10

11 **Abstract**

12 This article reports investigations on the anoxic corrosion process impacting a carbon steel/ultrapure
13 deaerated water system when it is exposed to gamma radiation (50 Gy h⁻¹), and on the associated
14 molecular hydrogen gas generation. On the one hand, a dynamic semi-open experimental setup allowing
15 to distinguish between the H₂ production related to water radiolysis and the one related to anoxic
16 corrosion has been adopted to estimate the corrosion rate associated to three successive temporal phases:
17 pre-irradiation, irradiation and post-irradiation phases. On the other hand, *post mortem* analyses
18 performed on both liquid and solid samples permitted to (i) quantify the chemical changes occurring in
19 solution due to the formation of water radiolysis products and (ii) observe and characterize the thin
20 corrosion layer composed of magnetite (Fe₃O₄) at the surface of the metallic coupons. We show that
21 gamma radiation induces a slight diminution of the carbon steel corrosion rate. However, by comparing
22 the mean corrosion rate values obtained for the three studied phases (i.e., before, during and after
23 irradiation), the chemical changes caused by radiolytic species seem to inhibit the formation of a thick
24 magnetite protective layer. Additionally, the corrosion rate observed in post-irradiation phase does not
25 decrease over time, which suggests that irradiation could modify the properties of the corrosion product

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26 layer by making it less protective. A structural modification of this oxide film might be caused by the
27 oxidizing water radiolysis products. Such mechanisms may favour continuous active corrosion
28 processes rather than passivation of the metallic surface and thus lead to a reduced lifetime of the
29 component.

30 **Keywords**

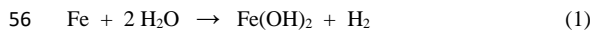
31 Anoxic corrosion; carbon steel; water radiolysis; γ -rays; hydrogen production

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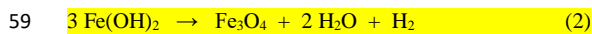
33 1. Introduction

34 Deep geological disposal of high-level radioactive waste (HLW) is foreseen by several countries to
35 protect living organisms from long-term radioactive contamination [1,2]. In France, according to the
36 multi-barrier concept developed by Andra (French radioactive waste management agency), HLW would
37 be embedded in a glass matrix cooled in a stainless steel container. This package would be then
38 encapsulated into cylindrical carbon steel overpack and inserted in a carbon steel casing tube within
39 horizontal micro-tunnel drilled in the highly impermeable Callovo-Oxfordian (COx) clay rock of the
40 Paris Basin [3,4]. A bentonitic cement-based grout material would be injected between the steel casing
41 and the host rock in order to (i) neutralize the acidity coming from pyrite oxidation in the COx while
42 preserving glass from detrimental highly alkaline media, (ii) limit oxygen diffusion and microbial
43 activity and (iii) passivate the steel casing. If carbon steel casing should ensure adequate mechanical
44 function over a century to allow the nuclear waste to be retrieved from the deep geological disposal
45 concept, carbon steel overpack must remain leakproof for a few thousand years to prevent natural clayey
46 porewater seeping from the host rock from reaching the vitrified waste during the thermal phase [4].
47 Throughout the duration of the operational phase of the project and long after the closure of the disposal
48 facility, several corrosion processes are expected to occur in a series of distinct environments (i.e., in
49 oxic or anoxic conditions, in contact with liquid or vapour phase solution, in contact with solution whose
50 chemical composition evolves over time due to the continuous percolation of clayey porewater through
51 the bentonitic cement grout material) which will gradually impair the carbon steel and finally induce
52 mechanical failure of the metallic component [5]. Predominant over the long term, carbon steel anoxic

53 corrosion process will progressively attack the metallic elements, with a mean corrosion rate value
54 between 0.1-10 $\mu\text{m year}^{-1}$ [3,6–8]. Under these conditions, iron will interact with water to produce
55 ferrous hydroxide ($\text{Fe}(\text{OH})_2$) and hydrogen gas (H_2):



57 When the Schikorr reaction (reaction 2) occurs, ferrous hydroxide ($\text{Fe}(\text{OH})_2$) can be then transformed
58 to the more thermodynamically stable magnetite (Fe_3O_4):



60 In natural or artificial porewater, or in presence of bentonite, iron can react with dissolved species to
61 form other corrosion products such as siderite (FeCO_3) through the overall reaction:



63 where M is a balancing univalent cation [9]. As shown in reactions (2) and (3), anoxic corrosion process
64 will produce magnetite and/or siderite as main corrosion products and generate significant amounts of
65 hydrogen. Thus, such anoxic corrosion processes induce corrosion products the formation of corrosion
66 products leading to the progressive protection of the metallic surface. However, this beneficial
67 phenomenon is always accompanied by the production of H_2 gas whose accumulation may significantly
68 affect mid- and long-term safety of the disposal facility. On the one hand, its high flammable and
69 explosive properties represent a risk during the operational phase and on the other hand, the consequent
70 overpressure is liable to lead to incomplete saturation of bentonite sealing plugs aiming at mitigating the
71 migration of radionuclides through disposal installation [5-9]. In addition, it is noteworthy that all these
72 corrosion processes will take place on carbon steel component exposed to ionizing radiations originating
73 from nuclear waste. These radiations will lead to the radiolysis of percolated porewater which forms
74 radiolytic species such as radicals (e_{aq}^- , H^\cdot , $\cdot\text{OH}$), molecular products (H_2O_2 , H_2) and ionic species
75 (H_3O^+), according to reaction (4) [10-11]:



77 These chemical species, whose concentrations are dependent on LET (Linear Energy Transfer, defined
78 as the amount of energy deposited by the charged particle along its path in solution) are prone to modify
79 the physico-chemical conditions at the metal-water interface, and thus to impact the corrosion processes
80 and the associated corrosion rate. Furthermore, these formed radiolytic species include H₂ gas, meaning
81 that porewater radiolysis will also lead to the additional production of this problematic gas [5,12-13].

82 Therefore, to contribute to the long-term safety assessment of such deep geological disposal, dedicated
83 research programs have been committed to study steel corrosion under irradiation and the associated
84 hydrogen gas production. The various experimental techniques that have been used to measure uniform
85 corrosion rates can be grouped as follow: weight loss measurements [13], hydrogen gas production
86 monitoring [14] and electrochemical measurements [15]. While a range of individual studies has been
87 performed to understand the impact of several parameters such as the dose rate (or total dose), the
88 temperature or the physico-chemical properties of the solution, the observed effects of ionizing radiation
89 on steel corrosion are still conflicting. Even though, most studies demonstrate that carbon steel corrosion
90 rate is enhanced by radiation exposure [13,16-17], some others tend to indicate the contrary [18–20]. In
91 parallel, while a large majority of the works cited above agreed on the fact that magnetite (Fe₃O₄) is the
92 predominant corrosion product which is formed under such experimental conditions, many key
93 questions regarding the mid and long term evolution of this oxide film properties, induced by the
94 physico-chemical modifications of the solution caused by irradiation, remain unanswered.

95 The primary motivation of the work presented in this article is to investigate the impact of gamma
96 radiation on carbon steel anoxic corrosion processes in order to (i) quantify the H₂ production and (ii)
97 estimate the associated corrosion rate allowing an optimisation of the metallic elements design. As an
98 initial approach, ultrapure deaerated water has been used in order to study a simplified system allowing
99 to capture the main radiolytic processes that could influence the corrosion processes. While almost all
100 studies dealing with the impact of ionizing radiations on steel corrosion processes have been performed
101 in closed systems, the present work is meant to get closer to the real disposal conditions by working in
102 a semi-open system. This experimental setup allows to distinguish between the H₂ production related to
103 water radiolysis and the one related to anoxic corrosion, making possible the estimation of associated

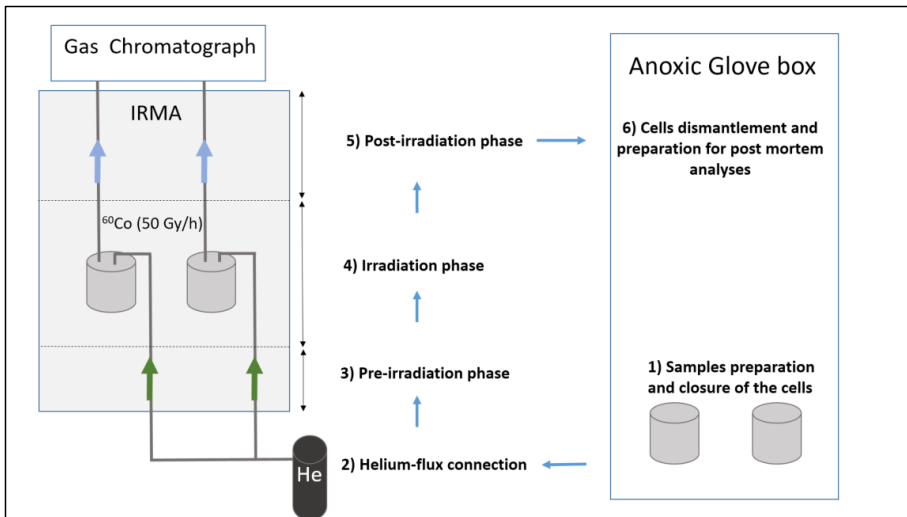
104 corrosion rate. Finally, *post mortem* analysis are performed on the metallic samples surface to identify
105 neoformed corrosion products, and chemical characteristics of the solution are determined.

106

107 2. Materials and Methods

108 2.1. Experimental setup

109 A schematic overview of the innovative dynamic experimental set up used in this work to study the
110 impact of gamma radiation on anoxic corrosion of steel processes is given in Figure 1. It allows to
111 differentiate the hydrogen production attributed to anoxic corrosion and the one imputed to radiolytic
112 process, by measuring continuously the H₂ gas generated by two parallel systems: one cell containing
113 six carbon steel samples immersed in pure deaerated water, the other cell containing only pure deaerated
114 water. These two stainless steel cells are placed into an irradiation chamber where they are exposed to
115 gamma-radiation and their H₂ evolution is recorded using in-line gas chromatography. This paper reports
116 the results associated with two successive series of experimental tests (Exp-A and Exp-B) where
117 hydrogen production is monitored before, during and after irradiation under anoxic conditions and at
118 ambient temperature.



119

120 **Fig. 1:** Schematic view of the experimental set-up and presentation of the adopted procedure, from the
121 preparation and closure of the cells until their dismantlement.

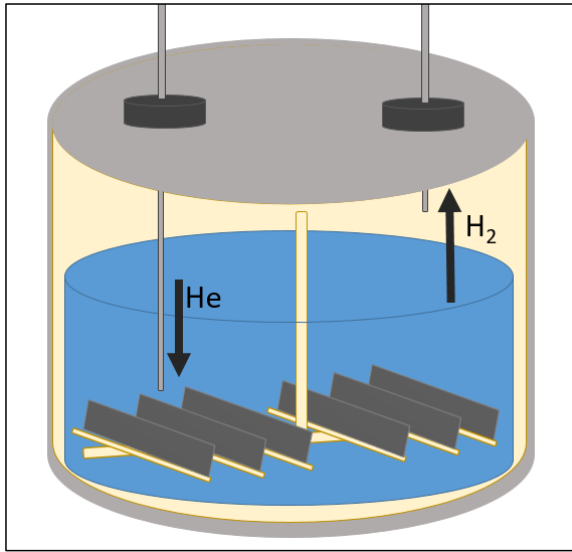
122

123 2.2. Experimental procedure

124 Corrosion experiments are performed on coupons (50 x 10 x 1 mm) of commercially available S235
125 carbon steel (max. 0.17 wt% of C, 1.40 wt% of Mn, 0.03 wt% of Sb, 0.02 wt% of P, 0.02 wt% of S). To
126 minimize the amount of surface oxide present before the start of Exp-A, four metallic samples are
127 roughly polished using #220 and #1200 SiC paper (“AR-coupons”), and two other samples are further
128 polished using diamond paste, obtaining a smooth mirror surface (“AP-coupons”). For Exp-B, the six
129 metallic samples are roughly polished (“BR-coupons”) with the same procedure described above. After
130 polishing, which takes place only few hours before the experiment, the samples are cleaned for 10
131 minutes with ethanol in an ultrasonic bath and then they are let to dry. For experimental system involving
132 metallic samples (A1-cell and B1-cell), the six coupons are inserted in a dedicated borosilicate glass
133 sample holder which allow to maximize the carbon steel surface available for corrosion processes. The
134 sample holder is then introduced in a borosilicate glass beaker containing a volume of 200 mL of
135 ultrapure (Millipore Alpha-Q with an electrical resistivity of 18.2 M Ω) deaerated water sufficient to
136 ensure a total immersion of the coupons. The beaker is then emplaced in a stainless steel cell made up
137 of a cylindrical body (10.4 cm, r=11cm) and a cover fitted with a tin seal allowing it to be hermetically
138 closed. The cell cover is fitted with two stainless steel line allowing the circulation of a carrier gas. The
139 input line has a sufficient length to get into the solution contained in the beaker whereas the output line
140 internal extremity is located at the same level as the beaker upper part (Figure 2). Both lines are equipped
141 with a valve on their external part to avoid any unintended oxygen contamination during cells
142 transportation. In parallel, experimental system dedicated to ultrapure deaerated water radiolysis study
143 (A2-cell and B2-cell) is prepared following the same procedural steps as in the case of experimental
144 system involving metallic samples, except the introduction of the sample holder containing the coupons.
145 To ensure that inert atmosphere prevail in our experimental cells and to avoid any further oxidation of
146 the metallic coupons, all these preparation processes are performed in an anoxic glove box under

147 continual nitrogen (N_2) flow. Once the cells are closed their tightness is checked via leak detector
148 (Leybold Inficon, UL 200).

149



150

151 **Fig. 2:** Schematic view of a stainless steel cell containing carbon steel samples (cell A1 & B1). Metallic
152 coupons, sample holder and pure deaerated water are placed into a glass beaker before entering the cell.

153

154 2.3. Irradiation experiments

155 Each experimental test involves two cells: a first one containing ultrapure deaerated water and metallic
156 samples and a second one containing only ultrapure deaerated water. After their preparation under inert
157 atmosphere, both cells are hermetically closed and carried from the glove box to the irradiation chamber
158 of IRMA (IRradiation MAterials) facility, of the Institute for Radiological Protection and Nuclear Safety
159 (IRSN), located at Saclay research center. The IRMA facility, by design, allows on-line measurements
160 during the irradiation phases. Thanks to the input/output lines, the cells are then connected to the
161 circulation system making possible to inject a carrier gas into the solution (input line) and to flow
162 continuously the produced hydrogen gas towards a gas chromatograph (output line) *via* flow-controllers,
163 set at 5 ml min^{-1} . In IRMA facility, materials are submitted to gamma radiation thanks to four cylindrical

164 sealed sources of ^{60}Co ($T_{1/2} = 5.27$ years). At the date of the experiments, the total activity of the sources
165 was about 774 TBq and 684TBq for Exp-A and Exp-B, respectively. In order to achieve an estimation
166 of the real conditions that would prevail in a repository environment, a rather low dose rate of 50 Gy h⁻¹
167 (corresponding to approximately five times to the predicted *in situ* dose rate) is applied. The
168 calculations of the theoretical distances between the sources and the cells, required to obtain the desired
169 dose rate, were carried out with a dedicated software (Microshield® 9.07). These distances are
170 afterwards validated by measuring the dose rate using a calibrated ionization chamber, at the defined
171 locations, in the presence of radioactive sources. Hence, the cells were placed about 1 m from the sources
172 support, behind a 5 cm width steel shield for Exp-A and a 2 cm width lead shield for Exp-B. For Exp-
173 A and Exp-B, the duration of the test under irradiation was 15 and 16 days respectively, corresponding
174 to a total absorbed dose of 18 and 20 kGy (in comparison with the 87660 kGy that a metallic component
175 should absorb over a period of 1000 years considering a reference dose rate of 10 Gy h⁻¹.

176

177 2.4. Hydrogen measurements

178 Hydrogen (H_2) is measured with a gas chromatograph VARIAN 450-GC. High purity helium is used as
179 the carrier gas with a pressure of 200 kPa. The analyzed gas sample volume is 1 mL. The column is a
180 Molecular Sieve 5A (length = 3m and diameter = 3.17 mm). The detection is performed using a Pulsed
181 Discharge Helium Ionization Detector (PDHID detector). The GALAXIE software (Galaxie
182 chromatography Data System) is used to collect data. Calibration of the detector is performed by
183 injection of a mixture of $\text{H}_2/\text{O}_2/\text{N}_2/\text{He}$ gas (gas mixture X50A, AirProducts) and uncertainty associated
184 to gas measurement is estimated to be less than 10%. Accordingly to a predetermined analytical
185 sequences, hydrogen production relative to each cell is independently measured every 20 minutes
186 before, during and after irradiation period. This measurement is performed on 1 mL of gas which is
187 sampled from the system and analysed by the gas chromatograph. Such measurement allowed to know
188 the exact amount of H_2 (ppm) contained in this 1 mL gas sample and after a conversion, one can obtain
189 the number of H_2 nanomoles present in this 1 mL gas sample. Since carrier gas (He) circulates at a flow
190 rate fixed at 5 mL min⁻¹, the number of H_2 nanomoles is multiplied by a factor 5 to obtain the number

191 of H₂ nanomoles generated by the experimental system during a 1-minute period (nmol min⁻¹). Once
192 irradiation phase stopped, cell containing only ultrapure deaerated water is disconnected from the
193 circulation system whereas cell containing metallic samples and ultrapure deaerated water remains
194 connected for some days more. Corrosion rate is estimated due to the precise measurement of molecular
195 hydrogen production in the cells. By subtracting the H₂ production associated to the cells containing
196 only pure deaerated water (cells A2 and B2) from the one generated by the cells containing pure
197 deaerated water and metallic samples (cells A1 and B1), it should permit to estimate the volume of
198 hydrogen generated only by the process of anoxic corrosion under irradiation during a 1-minute period
199 (nmol min⁻¹). At this point, it should be mentioned that the potential impact on H₂ production induced
200 by the additional water/glass surface interface arising from the sample holder, present only in the cells
201 A1 and B1, is assumed to be quite limited and is not considered in our calculation. The corresponding
202 number of H₂ nanomoles that are generated by our experimental system in a 1-year period (nmol year⁻¹)
203 is calculated and associated to the total surface area of our metallic samples to obtain the number of
204 H₂ nanomoles produced by the anoxic corrosion of the metallic coupons during a 1-year period (nmol
205 m⁻² year⁻¹). These H₂ production values (nmol m⁻² year⁻¹) are then converted in corrosion rate (μm year⁻¹)
206 values by using a conversion factor. This conversion factor is selected after the end of the experiment,
207 accordingly to the main corrosion product that is identified after structural characterization of the
208 sample's surface, as explained in previous study [21].

209 2.5. *Post mortem* analyses

210 At the end of the experimental tests, the cells are disconnected from the circulation system and moved
211 into the glove box to be dismantled in order to collect the carbon steel coupons and the solutions under
212 anoxic conditions.

213 2.5.1 Liquid samples

214 pH values of the solutions are measured immediately after the opening of the cells using a pH meter
215 (Multi 3420, WTW) with a glass electrode (ADA S7/IDS, WTW). For the solution collected in the cell
216 containing only ultrapure deaerated water, the concentration of hydrogen peroxide (H₂O₂) is determined

Commenté [LG1]: Lina's version

217 in less than 24 hours after the end of the irradiation phase with the Ghormley triiodide method [22]. Two
218 reagents are used: the first one is a mixture of potassium iodide (KI, VWR), potassium hydroxide (KOH,
219 Fluka) and ammonium heptamolybdate ((NH₄)₆Mo₇O₂₄, VWR), and the second one is a buffer mixture
220 (pH = 6) of potassium phthalate (C₈H₄K₂O₄, Merck) and phthalic acid (C₈H₆O₄, Merck). For a total
221 volume of 3 mL, 750 μL of both reagents are mixed with 1.5 mL of the sampled solution. After ten
222 minutes of reaction, the concentration of H₂O₂ is indirectly determined by measurement of I₃⁻ absorbance
223 with the UV-VIS spectrophotometer UV-2600 (Shimadzu). For the studied solution, at ambient
224 temperature, the molar extinction of I₃⁻ at the 348 nm wavelength is estimated at 25800 L mol⁻¹ cm⁻¹.
225 For the solution collected in the cell containing both ultrapure deaerated water and metallic samples, the
226 concentration of total dissolved iron (Fe_{tot}) is measured after acidification (HNO₃) by Inductively
227 Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), using a iCAP 7600 Duo (Thermo Electron)
228 apparatus. The concentration of silicon (Si) is also determined by ICP-AES.

229 2.5.2 Solid samples

230 During the dismantling of the experimental cell in the anoxic glove box, metallic coupons are collected,
231 rinsed with ethanol and dried to prevent post-oxidation. They are then introduced into airtight boxes
232 stocked inside the anoxic glove box. Out of the six coupons involved in each experimental test, two
233 coupons are dedicated to microstructural characterization, two other coupons are used for weight loss
234 measurement and corrosion rate estimation and the two last coupons are retained for additional analyses.
235 One should note that all the analysed metallic samples have been submitted to irradiation and that no
236 reference metallic sample (corroded without irradiation) has been studied in this work. Morphology and
237 chemical composition of the corrosion products formed at the surface of the carbon steel samples are
238 firstly investigated using a Scanning Electron Microscopy (SEM) coupled to Energy Dispersive
239 Spectroscopy (EDS). Analysis is performed using a Field Emission Gun (FEG) JSM7000-F SEM
240 apparatus (JEOL) under an accelerating voltage of 15 kV. Sample surface images are obtained using
241 both Secondary Electron (SE) mode and BackScattered Electron (BSE) mode. EDS spectra are collected
242 on point of interest using a silicon-drift detector (Bruker AXS). Samples are brought to the microscope
243 in an airtight anoxic box and all subsequent transfers are done rapidly (less than one minute) to minimize

244 exposure to oxygen. For optical imaging and micro-Raman (μ Raman) spectroscopy, metallic coupons
245 are kept in airtight anoxic box equipped with a 1 mm thick glass window. Samples surfaces are imaged
246 with an Olympus MX41 microscope equipped with a CCD camera. μ Raman spectra are obtained using
247 a LabRam HR800 spectrometer equipped with an Olympus MX41 microscope. YAG solid-state laser
248 with wavelengths of 532 and 785 nm are used as excitation sources and power outputs are kept at
249 reasonably low values ($\approx 500 \mu\text{W}/\mu\text{m}^2$) to limit thermal degradation.

250 2.5.3 Weight loss measurement

251 In the anoxic glove box, gravimetric measurements are performed on the dedicated metallic coupons
252 which have been initially weighted. At the end of the irradiation phase, these coupons are weighted
253 before and after being soaked in ultrasonic baths, with intermediate rinsing in deionized water between
254 each bath. This operation is repeated until the weight stabilization of the coupons. Such soaking stages
255 aim to remove the corrosion products present at the surface of the metallic sample without dissolving
256 carbon steel material. The solution contained in the bath is composed of 50% m distilled water + 50% m
257 HCl (37%, VMR) containing 5 g L^{-1} of hexamethylenetetramine ($(\text{CH}_2)_6\text{N}_4$, VMR) as an inhibitor of
258 iron dissolution under acidic conditions, and the duration of each bath is 5 minutes. The weight of the
259 coupons is measured using a high accuracy mass balance (XP205DR, METTLER TOLEDO) to allow
260 an estimate of the average general corrosion rate (r , in $\mu\text{m}/\text{y}$). The thickness (e , in μm) of metal damaged
261 by corrosion is calculated according to (5):

$$262 \quad e = \Delta m / (S \times \rho(\text{Fe})) \quad (5)$$

263 where S is the surface area, Δm is the mass difference, and $\rho(\text{Fe})$ is the iron density. The general
264 corrosion rate r is given by (6):

$$265 \quad r = e / t \quad (6)$$

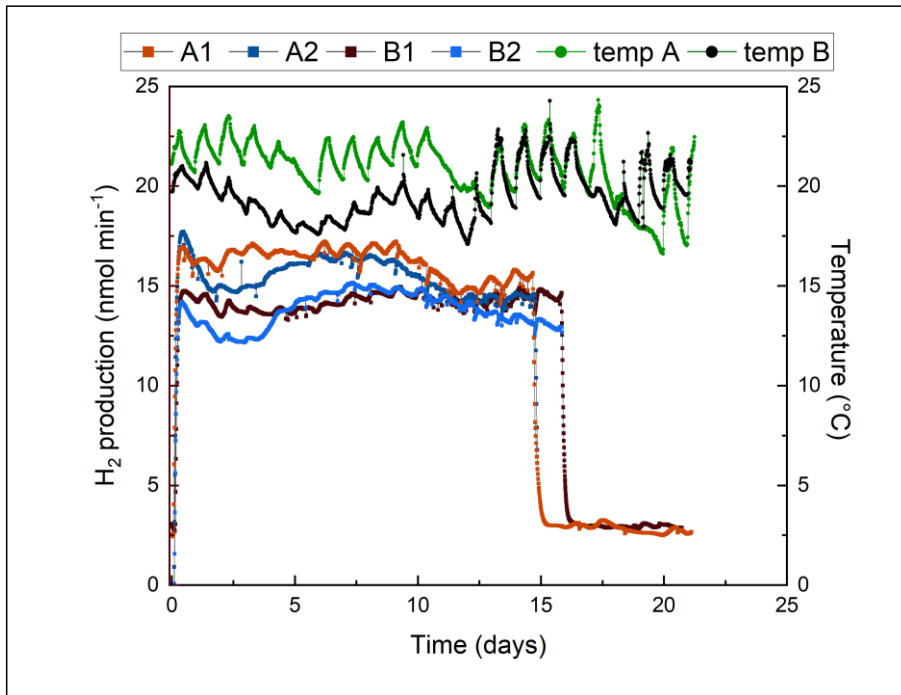
266 where t is time (in year).

267

268 3. Results

269 3.1. Hydrogen gas generation and corrosion rate measurements

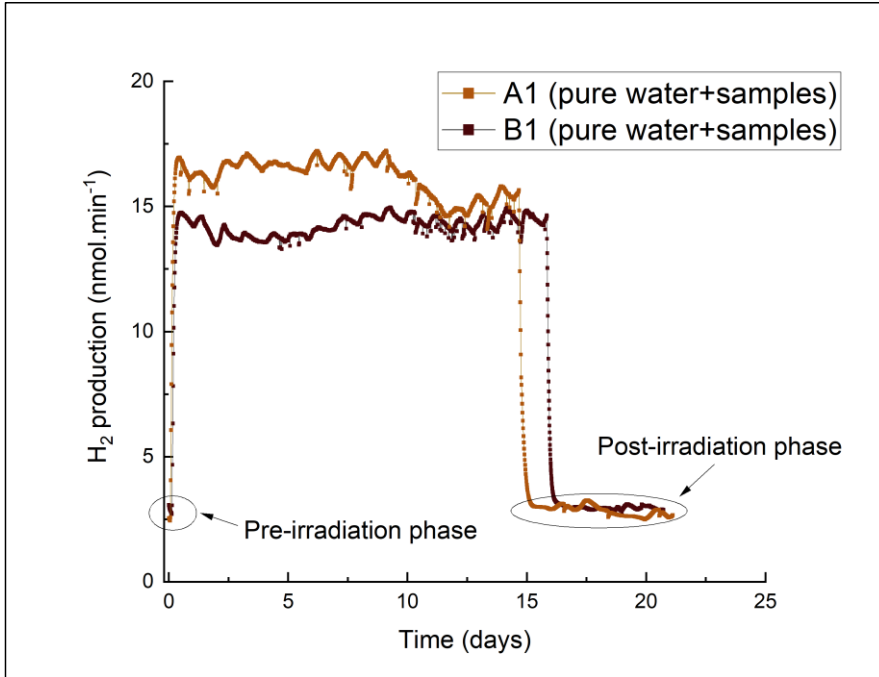
270 The evolution of hydrogen gas (H_2) production arising from the experimental cells tested during both
271 Exp-A and Exp-B are shown in Figure 3. The evolutions of the temperature measured in the IRMA



272 irradiation chamber during these two experiments are also reported in Figure 3. A comparison of the
273 hydrogen gas generation associated with the two cells containing carbon steel samples immersed in pure
274 deaerated water (A1-cell and B1-cell) is proposed in Figure 4.

275

276 **Fig. 3:** Hydrogen productions evolution measured during the three studied phases (before, during and
277 after irradiation) for experiments A and B with the associated temperature evolutions.



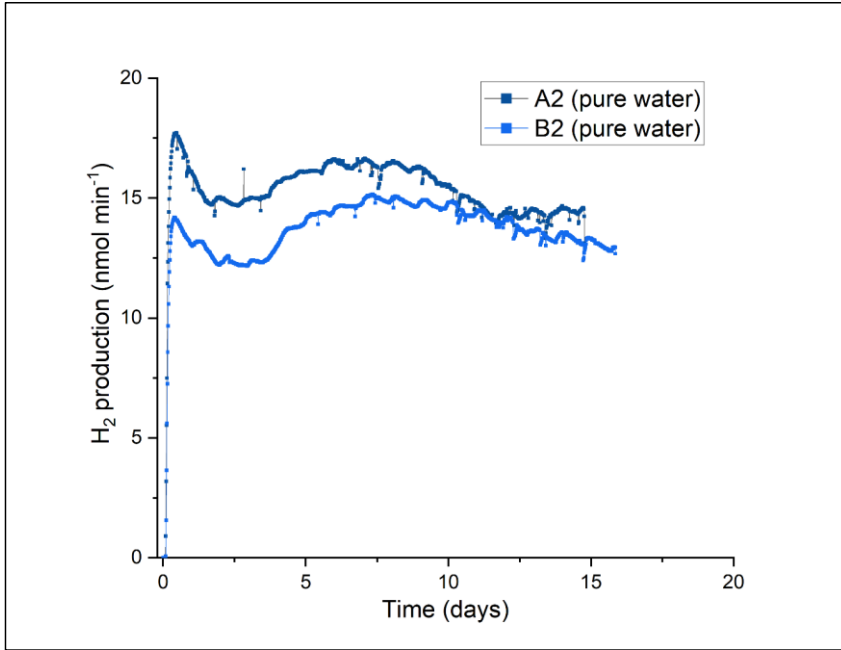
278

279 **Fig. 4:** Hydrogen productions evolution measured during the three studied phases (before, during and
 280 after irradiation) for cell A1 & B1 (ultrapure deaerated water and metallic samples).

281

282 For both cells, we can observe the very first H₂ production measurements performed before the
 283 irradiation phase that correspond to the hydrogen gas generated by carbon steel anoxic corrosion
 284 process. Then, the H₂ production measurements recorded during the irradiation phase correspond to the
 285 hydrogen gas generated by both water radiolysis and carbon steel anoxic corrosion processes. Finally,
 286 the last H₂ production results recorded after the irradiation phase correspond to the hydrogen gas
 287 generated by carbon steel anoxic corrosion process taking place post-irradiation. In parallel, Figure 5
 288 presents the evolutions of the hydrogen gas produced by the two cells containing only pure deaerated
 289 water (A2-cell and B2-cell), which is exclusively generated by water radiolysis.

290



291

292 **Fig. 5:** Hydrogen productions evolution measured during the three studied phases (before, during and
 293 after irradiation) for cell A2 & B2 (ultrapure deaerated water only).

294

295 For all cells, the average and maximum values of hydrogen gas produced during the three tested phases
 296 (i.e., before, during and after irradiation) are given in Table 1. Average and maximum corrosion rates
 297 determined from these hydrogen gas generation are presented in Table 2. Table 3 presents the corrosion
 298 rate values that have been calculated from weight loss measurements performed either on 2 metallic
 299 samples for experiment A or on 1 metallic sample for experiment B.

300

301

302

303

cell	H ₂ production before irradiation (nmol min ⁻¹)	H ₂ production during irradiation (nmol min ⁻¹)	H ₂ production post-irradiation (nmol min ⁻¹)
A1	2.5 ± 0.1	16.2 ± 0.7	2.8 ± 0.2
B1	2.8 ± 0.1	14.2 ± 0.4	3.0 ± 0.1
A2	0.0	15.4 ± 0.9	-
B2	0.0	13.8 ± 0.9	-

304
305 **Table 1:** Average values of H₂ production obtained for the three studied phases (before, during and after
306 irradiation) of experiments A and B.

307

corrosion rate via H ₂ gas measurements (µm year ⁻¹)		before irradiation	during irradiation	post-irradiation
A1	Average	1.1 ± 0.1	0.3 ± 0.4	1.2 ± 0.1
	Maximum	1.1	1.1	1.4
B1	Average	1.2 ± 0.1	0.2 ± 0.4	1.2 ± 0.1
	Maximum	1.2	0.8	1.3

308
309 **Table 2:** Mean corrosion rate values (obtained *via* H₂ production monitoring) for the three studied phases
310 (before, during and after irradiation) of experiments A and B.

311

corrosion rate <i>via</i> weight loss measurements (µm year ⁻¹)	
A1 (2 metallic samples)	4.8 (± 0.3)
B1 (1 metallic sample)	1.9 (± 0.3)

312
313 **Table 3:** Mean corrosion rate values (obtained *via* weight loss measurements) for experiments A and B.

314

315 3.2. *Post mortem* analyses

316 3.2.1 Liquid samples

317 Once the irradiation stops, cells A2 and B2 were dismantled in the anoxic glove box. Hydrogen peroxide
 318 (H_2O_2) concentration measurement was performed within 24 hours after the end of irradiation for cell-
 319 A2 only, and the associated result is $0.52 \times 10^{-6} \text{ mol L}^{-1}$. After the end of the experiment, A1 and B1
 320 were also dismantled in the anoxic glove box. The collected solutions, showed a slightly grey coloration,
 321 were analyzed to determine the quantity of the released dissolved iron. In cells A1 and B1 the dissolved
 322 iron was measured in comparable concentrations at 0.34 mmol L^{-1} and 0.25 mmol L^{-1} , respectively.
 323 Furthermore, the initial and final values of pH were recorded in the glove box for each cell just before
 324 their closure and just after their dismantling. All the above mentioned measurements results are
 325 summarized in Table 4.

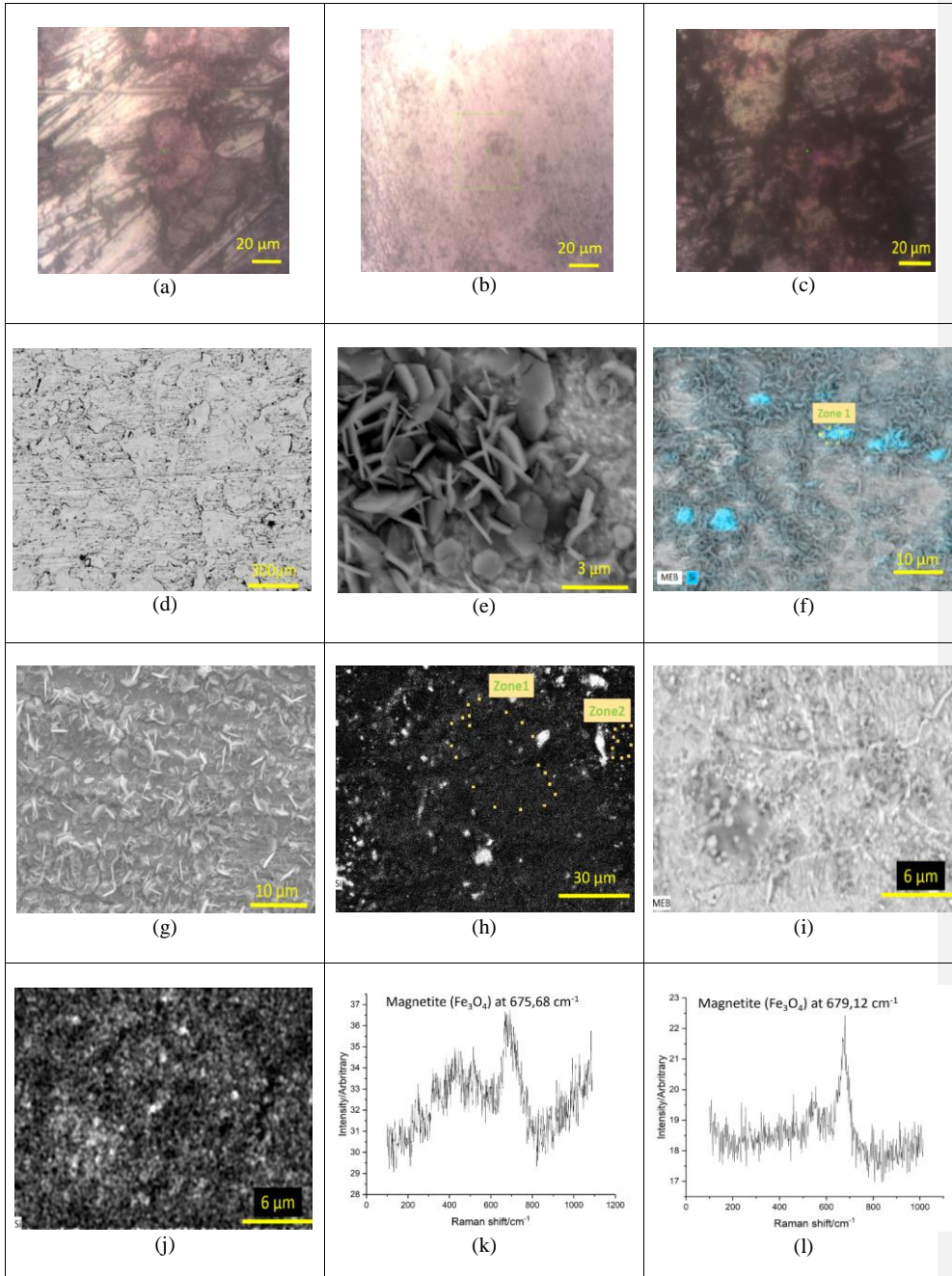
cells	initial pH (± 0.2)	final pH (± 0.2)	[Fe _{total}] (mmol L^{-1})	[H ₂ O ₂] ($\mu\text{mol L}^{-1}$)
A1	6.5	5.4	0.34 ± 0.01	-
B1	6.6	6.0	0.25 ± 0.07	-
A2	6.5	4.4	-	0.52 ± 0.09
B2	6.6	4.3	-	-

326
 327 **Table 4:** Overview of the solution chemical characteristics. Initial and final pH values, final total iron
 328 concentrations ([Fe_{total}]) and final hydrogen peroxide concentration ([H₂O₂]).

329

330 3.2.2 Solid samples

331 After the end of the experiment, carbon steel samples have been structurally characterized as it is
 332 depicted on Figure 6. Metallic coupons collected in cells A1 and B1 exhibited a darker appearance
 333 regarding their initial state. We observed that this coloration is even more intense at the samples' edges.
 334 In comparison with the "roughly polished" samples (AR and BR coupons), the "mirror surface" samples
 335 (AP coupons) present a blurrier surface. Unfortunately, the first observation shows that the short
 336 duration of our experiments does not permit the formation of a thick and significant corrosion layer, as
 337 illustrated by the slightly corroded surface observed by optical imaging on "AR-coupon" (Fig. 6a), "AP-
 338 coupon" (Fig. 6b) and "BR-coupon" (Fig 6c).



340 **Fig. 6:** Microstructural characterization of the carbon steel samples. Optical image of the corroded
 341 surface of AR-coupon (a), AP-coupon (b) and BR-coupon (c). SEM image in Backscattered Electron
 342 (BSE) mode of a roughly polished coupon before experiment (d), corroded surface of AR-coupon (e),
 343 corroded surface of BR-coupon (g) and corroded surface of AP-coupon (i). Composite BSE image –
 344 EDS elements map highlighting the areas enriched in Si on corroded surface of AR-coupon (f), corroded
 345 surface of BR-coupon (h) and corroded surface of AP-coupon (j). μ Raman spectrum collected on the
 346 corroded surface of AR-coupon (k) and on the corroded surface of AP-coupon (l).

347
 348 Surface examination using SEM-FEG microscopy have been performed on the surface of the metallic
 349 samples using Back Scattered Electron (BSE) as well as Secondary Electron (SE) mode. When
 350 comparing the initial surface of a roughly polished sample (Fig. 6d) with the final one of “AR-coupon”
 351 (Fig. 6e) and “BR-coupon” (fig 6g), we observe the formation of corrosion products mainly composed
 352 of hexagonal-shaped magnetite nanoplates. Surprisingly, such crystals formation has not been identified
 353 for “AP-coupon” (Fig 6i). Associated μ Raman analyses indicated the presence of magnetite (Fe_3O_4),
 354 with a characteristic peak at 675.68 cm^{-1} and at 679.12 cm^{-1} , as the only identified corrosion product for
 355 “AR-coupon” (Fig. 6k) and “AP-coupon” (Fig. 6l) respectively. On the other hand, it was not possible
 356 to identify any corrosion product for “BR-coupon”, even though, fine hexagonal-shaped formations
 357 observed in Fig. 6g. Moreover, it is worth mentioning that for both “AR-coupon” (Fig. 6f) and “BR-
 358 coupon” (Fig. 6h), elemental mapping revealed the presence of a significant amount of silicon (Table
 359 5).

Composition (at.%)						
	C	O	Na	Si	S	Fe
AR-coupon (zone 1)	6.6	51.2	0.2	11.9	0.1	29.9
BR-coupon (zone 1)	9.2	37.7	-	4.1	-	48.7
BR-coupon (zone 2)	12.4	13.3	-	0.1	2.2	72.0
AP-coupon	8.8	24.8	0.1	0.8	0.1	65.3

360
 361 **Table 5:** EDX analyses of selected zones for AR-coupon, BR-coupon and AP-coupon. Selected zones
 362 are illustrated in Fig. 6.

363

364 4. Discussion

365 This study made possible to assess the quantities of H₂ produced by two parallel systems (cell-1
366 containing six carbon steel samples immersed in pure deaerated water and cell-2 containing only pure
367 deaerated water) before, during and after irradiation under anoxic conditions and at ambient temperature.
368 Hydrogen productions associated to each system which have been measured during two successive
369 series of experimental tests (Exp-A and Exp-B) indicate quite reproducible results for the three studied
370 phases (before, during and after irradiation) (Fig.3), allowing us to validate our experimental setup.

371 Before irradiation, hydrogen production associated with the cells containing only pure deaerated water
372 (A2 and B2) remains zero, as expected (Fig.5). During this short pre-irradiation phase, the average H₂
373 production measured for the cells containing carbon steel samples (A1 and B1) is in the range of 2.5 -
374 2.8 x 10⁻⁹ mol min⁻¹ (Fig.4). These fluxes of hydrogen, which are generated only through anoxic
375 corrosion process, can be convert into corrosion rate values using a conversion factor [21] relevant for
376 anoxic corrosion mechanism leading to the formation of magnetite (Fe₃O₄) as main corrosion product
377 (*vide infra*). The corresponding calculated corrosion rate values range between 1.1 and 1.2 μm year⁻¹.

378 Such values are in good agreement with literature data obtained in anoxic conditions and at near neutral
379 pH, using ultrapure deaerated water [23], synthetic clay/granitic porewater [7-8], or numerical
380 simulation with porewater [24], for greater time scales.

381 Once the irradiation phase starts, water radiolysis process takes place in cells A2 and B2, and we can
382 immediately observe an intense production of H₂ (Fig.5). This is mainly due to recombination reactions
383 occurring between hydrogen radicals and hydrated electrons [25]. According to Pastina et al. [26] the
384 reactions (7), (8) and (9), which highlight the importance of hydrated electron (e_{aq}⁻) and H radical (H[•])
385 regarding molecular hydrogen formation, are responsible for the majority of H₂ formation:



Commenté [LG2]: Lina's version

389 Since we consider the case of gamma rays in this experiment, we assume these reactions occur in spurs
390 following the ionization processes [27]. As a result, G-values represent the primary yields of water
391 radiolysis species in the beginning of the homogeneous stage. The initial slope of the intense increase
392 of H₂ should correspond to the H₂ G-value, under γ -rays, $4.6 \times 10^{-8} \text{ mol J}^{-1}$ [28]. Using Figure 5 plots
393 for pure deaerated water and the experimental parameters (dose rate of 50 Gy h^{-1} , measured volume of
394 1 mL), we have determined the initial slope of H₂-formation. We obtained $5.03 \times 10^{-8} \text{ mol J}^{-1}$ and 4.48
395 $\times 10^{-8} \text{ mol J}^{-1}$ for A2 and B2 respectively, which roughly agrees with the literature. In parallel, H₂ can
396 be consumed by reacting towards $\cdot\text{OH}$ according to reaction (10):



398 but not in a big extent as this reaction is relatively slow and due to the fact that the use of a semi-open
399 system does not permit to H₂ gas to return to the liquid phase. A better explanation of the stabilization
400 of H₂ production is the accumulation in the solution of a radiolytic species which can efficiently react
401 with the precursors of H₂ i.e. e_{aq}^- and H atom as seen in reactions (7) to (9). This species in pure deaerated
402 water, under gamma rays, is H₂O₂, since O₂ cannot accumulate due to a constant He-bubbling.

403 Moreover, H₂O₂ can be formed as primary radiolytic species; but it can be also formed from HO₂ \cdot [29].
404 We can mention this eventuality in case of accidental inclusion of air in the system, since under gamma
405 rays HO₂ \cdot stems from the reaction of O₂ with e_{aq}^- . In deaerated water this mechanism is not relevant. The
406 only pathway to form HO₂ \cdot could be the reaction $\text{OH} + \text{H}_2\text{O}_2$ that in fine produces H₂O and O₂, which is
407 released into the atmosphere by bubbling. This might be relevant under high LET irradiation, e.g. alpha
408 rays, [29] in the case of a real deep geological repository.

409 As shown in Fig.5, H₂ productions successively measured for cells A2 and B2 indicate quite similar
410 evolution and correspond to average values of $15.4 \times 10^{-9} \text{ mol min}^{-1}$ and $13.8 \times 10^{-9} \text{ mol min}^{-1}$,
411 respectively. For both cells, the initial H₂ production peak related to the beginning of the irradiation
412 phase is followed by a sharp decrease taking place during the first 48h. After this, we observe a
413 stabilization phase (between day 2 and day 4) which is followed by a progressive increase (between day
414 4 and day 6) and then by a second stabilization period (between day 6 and day 10). The fact that the

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415 similar bell-shaped trends that we notice in H₂ trends in the absence of metal are not in accordance with
416 temperature evolution and there are not related to an accumulated pressure within the cell, makes us
417 conclude that they should be more attributed to a kind of regulation, considering the presence of possible
418 impurities. Impurities arising from anything in contact with the pure water solution could lead to
419 interaction of very reactive radicals e.g., ·OH and this could impact hydrogen production, as the
420 maintenance of a totally ultra-pure water system in practice is almost impossible. Finally, both cells
421 display a progressive decrease of their H₂ production until the end of the irradiation phase. According
422 to the literature, a possible explanation for this progressive H₂ decrease arises from the formation of
423 other radiolytic products with compatible reaction rates. The major factor that could inhibit H₂ formation
424 is the presence of hydrogen peroxide (H₂O₂). The latter, as its concentration rises, is able to scavenge
425 the main precursor of hydrogen, i.e. the hydrated electron (e_{aq}⁻) [30], as shown by reaction (11):



427 and thus, to inhibit the formation of molecular hydrogen. H₂O₂ was still identified in solution after a few
428 hours necessary to collect sample in the cell A2 just after the end of irradiation. This low concentration
429 (H₂O₂ = 0.52 × 10⁻⁶ mol L⁻¹, see Table 4) is the H₂O₂ concentration remaining in solution after
430 irradiation. Then it suggests that reaction (11) occurred during irradiation.

431 Even if it seems that the H₂ production is influenced by the temperature fluctuations (Fig.3), it is
432 somehow difficult to definitely state on the real impact of temperature on hydrogen production. On the
433 one hand, the decrease of the temperature recorded between day 11 and day 13 for Exp-A seems to
434 induce a diminution of the H₂ produced in cell A2. On the other hand, the increase of H₂ production
435 observed between day 4 and day 6 takes place during a temperature decrease suggesting that temperature
436 has no strong impact on radiolytic hydrogen production, as it has been previously mentioned [25]. The
437 hypothetical coupled fluctuation of both H₂ production and temperature values observed on Fig.3 is indeed
438 due to an experimental artefact induced by the great sensitivity of the gas chromatograph PDHID
439 detector to temperature variation. If such perturbation could modify somehow the values of H₂
440 production, it impacts the two studied cells in parallel and should not have any effect on the derived
441 corrosion rate values.

442 As shown in Fig.4, hydrogen productions associated to cells A1 and B1 are also strongly impacted by
443 the irradiation. Indeed, the volume of H₂ generated by anoxic corrosion of the carbon steel samples is
444 added to the one produced by water radiolysis process. Hydrogen productions successively measured
445 for cells A1 and B1 indicate quite similar evolution and correspond to average values of 16.2×10^{-9} mol
446 min⁻¹ and 14.2×10^{-9} mol min⁻¹, respectively. This could be due to the fact that Fe-ions are known for
447 reacting with radiolytical species with competitive reactions and thus they are able to impact H₂
448 evolution. Fe-ions can scavenge H₂ precursors (e_{aq}⁻) and thus lead to a H₂ decrease, but at the same time
449 Fe-ions can also interact very fast with OH radical, inhibiting the probability of reaction (11) and
450 promote an H₂ increase. Therefore, we could say that an overall outcome would be a more stable H₂
451 evolution over time in the presence of metallic surfaces. By subtracting H₂ production associated to the
452 cells containing only pure deaerated water (cells A2 and B2) from the one generated by the cells
453 containing pure deaerated water and metallic samples (cells A1 and B1), it should permit to estimate the
454 volume of hydrogen generated only by anoxic corrosion process. Thus, the average corrosion rates
455 calculated for A1 and B1 during the irradiation phase are 0.3 μm year⁻¹ and 0.2 μm year⁻¹, respectively.
456 These corrosion rate values obtained under irradiation and for anoxic conditions are consistent with the
457 ones in previous studies performed in such experimental conditions [14,23]. Furthermore, we observe
458 that cells A1 and B1 display constant behaviors all along the irradiation phase without any significant
459 corrosion rate increase. This stabilization may be attributed to the gradual formation of a thin corrosion
460 product layer, mainly composed of magnetite as observed during the structural characterization of our
461 samples (Fig.6), which passivate and protect the carbon steel coupons surface. The identification of
462 magnetite as predominant corrosion product has previously been observed in several carbon steel anoxic
463 corrosion studies performed either under un-irradiated conditions [6,8,9,31–34] or under irradiation
464 [14,23,35–37]. In previous studies dealing with long term anoxic corrosion under irradiation [14,38]
465 such progressive magnetite formation has been associated to corrosion rate decrease. On the other hand,
466 the comparison between corrosion rate values obtained during irradiation (0.3-0.2 μm year⁻¹) and the
467 ones gained during the short pre-irradiation phase (1.1-1.2 μm year⁻¹) suggests that the presence of
468 gamma radiation inhibits the anoxic corrosion rate of carbon steel. This is in contradiction with studies

Commenté [LG4]: Addition by linas version comment 33

469 comparing irradiated and un-irradiated samples [13,14,16,17,23] suggesting that ionizing radiation leads
470 to a clear enhancement of the corrosion rate.

471 As soon as irradiation stops, hydrogen production associated to cells A1 and B1 falls until its
472 stabilization at values around 2.8×10^{-9} mol min⁻¹ and 3.0×10^{-9} mol min⁻¹, respectively (Fig.4). These
473 volumes of hydrogen are generated only through anoxic corrosion process, and they allow to calculate
474 corresponding anoxic corrosion rate, approximately at 1.2 $\mu\text{m year}^{-1}$ for both experiments. When
475 comparing these results with the ones obtained during the pre-irradiation phase, we do not observe any
476 diminution suggesting that, despite the primary and partial formation of a thin magnetite layer on the
477 surface of the metallic samples, anoxic corrosion process continues to operate at the same rate that as
478 before irradiation. This could be due to a progressive alteration of the primary formed magnetite layer
479 which no longer protects the metal surface from further corrosion. The alteration could be caused by
480 radiolytic-induced modifications of the solution. For example, the acidification of the solutions
481 contained in cells A1 and B1 (see Table 4) could be due to the fact that under irradiation hydronium
482 ions are produced in larger quantities than hydroxide ions. In the modelling work performed by Lapuerta
483 [39], to explain the pH decrease that she observed experimentally (from 6.5 to 4.5), the author used
484 primary radiolytical yields of α -rays ($g(\text{H}^+) = 0.37 \times 10^{-7}$ mol J⁻¹ and $g(\text{OH}^-) = 0.06 \times 10^{-7}$ mol J⁻¹)
485 corresponding to a mean LET value associated to a 2 MeV proton. Similarly, Christensen & Bjergbakke
486 [40], propose primary radiolytical yields for low LET associated to gamma radiation with values at 2.85
487 $\times 10^{-7}$ mol J⁻¹ and 0.10×10^{-7} mol J⁻¹ for H⁺ and OH⁻, respectively. However, simulation results show
488 that the H⁺ concentration increase is not sufficient and the author proposed the contribution of additional
489 ferrous/ferric ions hydrolysis processes to explain the observed pH diminution [39]. Additionally, the
490 pH decrease due to the radiolytic oxidation of ferrous ions under gamma irradiation is also confirmed
491 by Sutherland et al. [41]. Moreover, focusing on the final pH value on cells A1, B1 we should have in
492 mind that our pH measurements have been performed several days after the end of irradiation phase.
493 Once irradiation stops, the concentration of radiolytic species is dramatically decreased, although, the
494 most stable among them, is hydrogen peroxide (H₂O₂), able to oxidize ferrous ions available in bulk
495 solution via Fenton reaction (12):



497 During post-irradiation phase, this reaction will generate hydroxide ions prone to contribute to the higher
498 final pH values, compared with the pH values measured in the cells where there were no metallic
499 samples. Hence, the measured acidification of the solution is lower in in the presence of iron compared
500 to the one's measured in the cells with pure water, however, it could be sufficient enough to impact
501 corrosion processes.

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502 Such acidification of the solution can affect the magnetite solubility and thus inhibits the formation of a
503 significant corrosion product layer which would lead to a corrosion rate decrease. This observation is to
504 put in perspective with the work of Daub [42], showing that, contrary to the un-irradiated samples
505 exhibiting a constant oxide film growth, the magnetite film thickness obtained on the gamma-irradiated
506 sample displayed an initial fast development and then rapidly stabilized over time. On the other hand,
507 impact of ionizing radiations on corrosion process can also be attributed to the oxidizing water radiolysis
508 products such (H_2O_2 , O_2 or $\cdot\text{OH}$) which are produced simultaneously with reducing water radiolysis
509 species (H_2 , e_{aq}^-). Their interactions with carbon steel and stainless steel are known to induce a metal
510 corrosion potential increase, as has been described by an electrochemical study [15]. Demonstrating that
511 even after the end of the irradiation, the corrosion potential of the steel did not return to its initial lower
512 pre-irradiated value, this work also pointed out the possible long-term changes in the corrosion product
513 layer properties induced by structural modification of the oxide film (e.g., aggregation and coarsening
514 of magnetite particles caused by the continuous dissolution-precipitation processes induced by
515 irradiation as it is proposed by Sutherland et al. [41]). Such deterioration could impact the porosity of
516 the neoformed corrosion product layer and may lead to a less active passivation of the metal.

517 In parallel, other parameters linked to our experimental setup can potentially impact the stability of the
518 neoformed magnetite layer. If we refer to the work of Brusch & Pearl [31], highlighting the almost linear
519 dependence of corrosion rate on the velocity of the tested flowing system, one can imagine that the 5
520 mL min^{-1} flow rate used into our gas circulation system may participate to the constant removal of the
521 corrosion product located at the liquid/solid interface.

522 In addition, it was pointed out by Platts et al. [9], that any loss of ferrous ions from the system, e.g. from
523 either adsorption and/or precipitation phenomena, can impair the formation of a thick protective
524 corrosion product layer and lead to a renewed corrosion process.

525 Due to the progressive glass alteration process, the use of glass beaker and glass sample holder may
526 induce ion-exchange mechanisms between silicon and iron ions [44–46]. We thus decided to perform
527 additional post-mortem analysis on these glass elements. Acidic attack realized on glass beakers showed
528 that total iron concentration value obtained for A1 beaker is two orders of magnitude higher than the
529 one associated to the pristine beaker, meaning that ferrous iron ions have been entrapped in the glass
530 alteration layer as observed in previous studies [47,48]. This ion exchange between iron and silicon is
531 further confirmed by both the presence of silicon on the surface of the metallic coupons (Fig. 6 and
532 Table 5), and the presence of silicon in solutions collected in A1 and B1 cells (results not shown).

533 From a radiolytical point of view, the densification of the borosilicate glass under gamma irradiation
534 has been described in previous studies [49–52] to be a dose rate and boron content dependent process.
535 In parallel, one can note that previous studies [53–55] showed that radiolytic yield of H₂ can be impacted
536 in the case of oxide/water interfaces. Moreover, Schatz et al. [56], pointed out the fact that, during
537 experiments dealing with silica suspensions under irradiation, the absorbed energy by silica
538 nanoparticles crosses the solid/liquid interface and generates hydrated electrons in the aqueous phase as
539 a result of an interfacial charge transfer process. This observation is in good agreement with the work
540 of Nakashima & Tachikawa [57], where is mentioned the possible mechanism for hydrogen production
541 by energy transfer from silica to the aqueous solution. The authors mention that a part of the initial
542 hole/electron formation from irradiated silica can migrate in solids and reach the surface where they
543 excite physisorbed water, leading to hydrogen formation. Therefore, we should note these parallel
544 mechanisms potentially able to moderately affect hydrogen production arising from our experimental
545 set-up involving irradiated glass. However, considering the low silica concentrations measured in our
546 solutions, we consider that such processes involving silica nanoparticles should not significantly impact
547 H₂ production.

548 Regarding the corrosion rates values estimated by weight loss measurements ($4.8 \mu\text{m year}^{-1}$ for A test
549 and $1.9 \mu\text{m year}^{-1}$ for B test, see table 3), we observe that they are in the same order of magnitude as the
550 ones obtained during previous studies using the same technique [13,23]. Nevertheless, as mentioned in
551 previous studies [58–60] corrosion rates exported from weight loss measurements are higher than the
552 ones derived from the hydrogen gas generation measurements. Even though it is difficult to compare
553 instantaneous corrosion rate values obtained by H_2 gas generation monitoring with average corrosion
554 rate by weight loss measurements, such discrepancy would highlight that these two methods do not
555 monitor the same process. Moreover, one should mention that despite the anoxic conditions prevailing
556 in our experimental set-up, water radiolysis induced the production of reducing (H_2 , e_{aq}^-) as well as
557 oxidizing (H_2O_2 , $\cdot\text{OH}$, O_2) species prone to modify locally physico-chemical conditions and to promote
558 in some extent oxidic corrosion processes that are not associated to any H_2 gas production and for this
559 reason, they are not considered by our experimental approach which is based on H_2 monitoring.
560 Consideration of such information should support the concept of anoxic corrosion experiments based
561 on a twofold approach combining H_2 monitoring and weight loss measurements methods.

562 5. Conclusion

563 This work provides new insights on the impact of gamma radiation on carbon steel anoxic corrosion
564 process and on the associated H_2 gas generation. We adopted an experimental set-up based on the
565 hydrogen gas production monitoring which allows to distinguish between the H_2 production related to
566 water radiolysis and the one related to anoxic corrosion, making possible the estimation of associated
567 corrosion rate. Contrary to numerous previous results found in the literature, the first observation is that
568 gamma radiation does not induce a clear increase of the carbon steel corrosion rate but rather to slightly
569 inhibit it. This is probably due to the gradual formation of a thin magnetite layer which partially
570 passivates and protects the metallic surface. The second observation concerns the properties of
571 associated with such the magnetite layer and their evolution, during and after irradiation. Even though
572 corrosion rate under irradiation appears to be lower, the redox modifications of the solution induced by
573 radiolytic species production can induce the progressive alteration of the magnetite layer. This passive
574 film deterioration may maintain the metal surface in an active corrosion mode for longer period of time.
575 In parallel, the fact that the corrosion rate observed post-irradiation does not differ from the one

576 measured before irradiation also suggests the possible progressive degradation of the passivating
577 corrosion product layer. This degradation could be due to oxidizing water radiolysis products which can
578 induce structural modifications of the oxide film, either directly or through local modification of the
579 physico-chemical conditions of the solution. If such sustained corrosion processes are verified, it could
580 impact the degradation kinetic and the durability of metallic components used for HLW disposal gallery.
581 Nevertheless, these assumptions need to be confirmed by further investigations performed with longer
582 irradiation period and with more representative solutions (clayey pore water, alkaline pore water) in
583 order to acquire an accurate understanding of gamma radiation impact on corrosion product growth and
584 also on the evolution of oxide film properties. In parallel, numerical simulations should help to predict
585 the concentration evolution associated to key radiolytic species prone to impact anoxic corrosion under
586 irradiation processes and to better understand the effect of ionizing radiation in presence of metal/water
587 interface or metal/oxide/water interface.

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590

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