FORGE Work Package 2 Final Report - Experimental Studies on Hydrogen Generation by Corrosion

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<table>
<thead>
<tr>
<th>Authorised by</th>
<th>Name</th>
<th>Organisation</th>
<th>Signature</th>
<th>Date</th>
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<tbody>
<tr>
<td></td>
<td>D. Dobrev</td>
<td>UJV (Czech Rep.)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>D. Stammose</td>
<td>IRSN (France)</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>D. Pellegrini, WP2 Leader</td>
<td>IRSN (France)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>A. Vokal</td>
<td>UJV (Czech Rep.)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Verified by</td>
<td>S. Norris</td>
<td>NDA RWMD (UK)</td>
<td></td>
<td>27/1/14</td>
</tr>
<tr>
<td>Approved by</td>
<td>R. Shaw</td>
<td>NERC BGS (UK)</td>
<td></td>
<td>3/2/14</td>
</tr>
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</table>

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Fate of repository gases (FORGE)

The multiple barrier concept is the cornerstone of all proposed schemes for underground disposal of radioactive wastes. The concept invokes a series of barriers, both engineered and natural, between the waste and the surface. Achieving this concept is the primary objective of all disposal programmes, from site appraisal and characterisation to repository design and construction. However, the performance of the repository as a whole (waste, buffer, engineering disturbed zone, host rock), and in particular its gas transport properties, are still poorly understood. Issues still to be adequately examined that relate to understanding basic processes include: dilational versus visco-capillary flow mechanisms; long-term integrity of seals, in particular gas flow along contacts; role of the EDZ as a conduit for preferential flow; laboratory to field up-scaling. Understanding gas generation and migration is thus vital in the quantitative assessment of repositories and is the focus of the research in this integrated, multi-disciplinary project. The FORGE project is a pan-European project with links to international radioactive waste management organisations, regulators and academia, specifically designed to tackle the key research issues associated with the generation and movement of repository gasses. Of particular importance are the long-term performance of bentonite buffers, plastic clays, indurated mudrocks and crystalline formations. Further experimental data are required to reduce uncertainty relating to the quantitative treatment of gas in performance assessment. FORGE will address these issues through a series of laboratory and field-scale experiments, including the development of new methods for up-scaling allowing the optimisation of concepts through detailed scenario analysis. The FORGE partners are committed to training and CPD through a broad portfolio of training opportunities and initiatives which form a significant part of the project.

Further details on the FORGE project and its outcomes can be accessed at www.FORGEproject.org.

Contact details:

EC FORGE Work Package 2 Leader:

Dr Delphine PELLEGRINI
Organisation: IRSN
Tel: 33 (1) 58 35 74 53
Fax 33 (1) 58 35 79 76
email: delphine.pellegrini@irsn.fr
web address: www.irsn.fr
Address: 31 avenue de la Division Leclerc
92260 Fontenay aux Roses Cedex
FRANCE
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Summary

In the framework of the safety assessment of a radioactive waste geological disposal, one of the issues of concern is the impact of gases produced within the facility, notably in terms of possible perturbations which may decrease the containment capability of the disposal system. The integrated, multi-disciplinary FORGE project addresses this key research area so as to provide new insights into the processes and mechanisms governing gas generation and migration.

The gas production rates from corrosion are strongly influenced by the specific conditions in the repository, thus the corrosion evolutionary path, which describes processes such as oxygen consumption, radiolysis, salinity changes, pH changes and temperature evolution, must be clearly defined as a basis for establishing the hydrogen gas production rates to be used in safety assessments.

Considerable progress was made prior to the FORGE project in the area of determining hydrogen gas production associated with anaerobic corrosion of metals. There are nonetheless some conditions for which further study may be required, as differences in repository design concepts can influence the gas evolution rates. Thus, a specific Work Package (WP2) of the FORGE project dealt with the effects of redox, temperature, presence of bentonite and gamma radiation on hydrogen generation and associated corrosion of carbon steels in clay pore water.

WP2 studies of the long-term corrosion rate, i.e. the steady-state rate, show that the corrosion rate is a few µm/a in bentonite pore water. In compacted bentonite, the initial corrosion rate is greatly accelerated (up to tens of µm/a) in the first month compared to the rate in bentonite pore water. The increased rates are thought to be due to enhanced dissolution of the protective film on the steel as a result of sorption of Fe(II) onto the bentonite. As the effect of compacted bentonite is expected to decrease with time, this may be consistent with other prior studies, which recommend considering a rate of a few µm/a. Other WP2 findings show that the initial corrosion rate of carbon steel is significantly higher at elevated temperature (70°C) than at lower temperatures, but the rate decreases rapidly and there is no significant temperature dependence after approximately one month. As a result, the higher initial hydrogen production rate is not likely to be important from a long-term performance assessment perspective.

Additional studies in WP2 found that gamma radiation at dose rates in the range of 11-100 Gy/h either enhances or decreases both hydrogen production and the corrosion rate of carbon steel. Furthermore, the enhancement of the rate was sustained even after irradiation ceased, the reasons for which are not yet fully understood. The studies may be relevant to some disposal concepts, but cannot be extrapolated to other conditions (e.g. lower dose rates or the presence of clay).

A process that may be relevant to corrosion and hydrogen generation is microbial corrosion. This was not studied in FORGE, but received some attention in prior laboratory studies. Further in situ studies may be warranted.

The approach to modelling gas generation for safety assessments includes some simplifications that need to be checked depending on the application of the modelling. For example, higher short-term gas production rates are often not considered in long-term calculations of gas build-up, as the amount of gas produced is very small relative to the total produced over tens of thousands of years. However, in some cases, for example determining if there are any effects from short-term gas transients, this may not be appropriate and must be checked for the specific EBS design and hydraulic boundary conditions.
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1 Introduction

In the framework of the safety assessment of a geological disposal, one of the issues of concern is the impact of gases produced within the facility, notably in terms of possible perturbations (modification of the water saturation process, fracturing of the host-rock or of engineered components, opening of interfaces...) which may decrease the containment capability of the disposal system. The integrated, multi-disciplinary FORGE project addresses this key research area so as to provide new insights into the processes and mechanisms governing gas generation and migration.

The assessment of kinetics of gas production/consumption close to the point of origin is an important input in the understanding of the likelihood of the development of a discrete phase and of the global evolution of hydrogen within the repository. The main source of gas in a geological disposal of High Level Waste (HLW) is generally the formation of hydrogen by corrosion of ferrous materials (although it may depend on waste types and disposal design). Thus, a specific work package (WP2) within the FORGE project addresses the generation of hydrogen. It has been focused on the hydrogen source term from corrosion of carbon steel components such as mechanical supports or overpacks.

Actually, the state-of-the-art drawn at the onset of the project (see Stammose and Vokal, 2012a) showed that very high hydrogen generation rates (about 20 mol.m\(^{-2}\).yr\(^{-1}\)) can be reached at the beginning of corrosion until a corrosion layer is formed on the metal surface. After some time corrosion rate will decrease to much lower values, certainly below 5 μm/yr, which corresponds to hydrogen generation rates lower than 1 mol.m\(^{-2}\).yr\(^{-1}\). However this review confirmed that, despite the work already done to study iron and carbon steel corrosion mechanisms under various conditions, uncertainties still remained concerning in particular, the effect of content in oxygen, temperature, and chemistry of water and/or solids in presence on corrosion and thus on hydrogen production rates. Besides, there were very little results available on the impact of radiation on corrosion in anaerobic conditions and on hydrogen production/consumption. These data tended to indicate that the corrosion of carbon steel is enhanced under irradiation, but the processes as well as the quantification were still uncertain.

Thus, the evolution of the hydrogen generation rate within a repository due to corrosion of carbon steel components - i.e. the intensity and duration of the “transient” and “steady state” of hydrogen production rate - deserves a greater understanding of the underlying mechanisms. The main expected outcome from WP2 was a better assessment of the effects of these key parameters (T, Eh, reactive surface, solid and/or liquid phases in contact with steel, radiation...) representative of repository conditions, on corrosion rates and consequently on hydrogen production rates. For this purpose both WP2 partners, UJV (Ustav Jaderneho Vyskumu, Czech Republic Nuclear Research Institute) and IRSN (Institut de Radioprotection et de Sûreté Nucléaire, French Technical Safety Organization), have carried out experiments under various conditions, which address these specific issues related to corrosion.

The present WP2 final deliverable WP2 documents the main experiments carried out by the two WP2 partners, further details on the whole experimental program being reported in intermediate FORGE deliverables (see Brůha, 2010; Stammose and Vokal, 2012b, 2013). The main outcomes drawn on the basis of the whole program are presented in a last chapter.
2 UJV Experiments

2.1 EXPERIMENTAL METHODS

The first corrosion system consisted of 1 or 10 carbon steel plates in 2 L of synthetic bentonite pore water. The carbon steel correspond to the Czech standard ČSN ISO 11321 (Table 1). The dimension of the plate was 70x70x1 mm with circle cut out in center of diameter 8 mm; the surface of carbon steel plates was 99.7 cm$^2$/plate. Before the experiment carbon steel plates were polished by sandpaper of grid 600 and washed by ethanol.

The second corrosion system consisted of 30 g or 5 g of iron powder in 2 L of synthetic bentonite pore water. The iron powder was Alfa Aesar A Johnson Matthey Company (< 10 micron, 99.9+% (metal basis), and surface 0.205 m$^2$/g).

Table 1 Composition of carbon steel ČSN ISO 11321

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>O</th>
<th>Si</th>
<th>Ca</th>
<th>Mn</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>2.17</td>
<td>1.81</td>
<td>0.39</td>
<td>0.28</td>
<td>0.45</td>
<td>94.89</td>
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The third corrosion system consisted of carbon steel sample (standard EN 10204/3.1) of cylindrical form (surface 141 cm$^2$) in 300 ml of synthetic bentonite pore water. The layer of carbon steel sample affected possibly by atmospheric oxidation or non-uniform surface was removed by lathe before the experiment and the carbon steel sample was washed by ethanol. The content of impurities in the carbon steel of this standard is given in the following Table 2. An additional set of experiments was carried out with direct contact between solid bentonite (thickness 20 mm, diameter 100 mm) and carbon steel sample (material ČSN ISO 11321, diameter 92.4). Bentonite was either compacted to density of 1600 kg/m$^3$ (1 experiment), bubbled with nitrogen, and saturated by synthetic granitic water under pressure of 5 MPa (backpressure of 5 MPa was held by Haskel pump), or not compacted (3 experiments) with the same treatment but saturated under the atmospheric pressure. Temperature of the carbon steel sample was controlled at 70 °C. In that case, the average hydrogen production rate was calculated from the weight changes of carbon steel sample before and after corrosion (while in experiments without solid bentonite, a continuous monitoring of hydrogen production was used).

Table 2 Composition of carbon steel EN 10204/3.1

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>P</th>
<th>Mn</th>
<th>S</th>
</tr>
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<tr>
<td>%</td>
<td>0.1</td>
<td>0.035</td>
<td>0.45</td>
<td>0.035</td>
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Most of the experiments were conducted in the synthetic bentonite pore water (Van Loon et al., 2005) with composition of and quantity of chemicals used for its preparation given Table 3. The pH of this water was 7.5, conductivity 2100 mS.m$^{-1}$, and ionic strength 0.29 mol.l$^{-1}$. The synthetic bentonite pore water was systematically inserted into an anaerobic box 14 days (minimally) before starting experiment for consumption of traces of oxygen.
Table 3: Compositions and chemicals for preparation of synthetic bentonite water

<table>
<thead>
<tr>
<th>Salt</th>
<th>m [g.l⁻¹]</th>
<th>ion</th>
<th>m [mol.l⁻¹]</th>
</tr>
</thead>
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<tr>
<td>NaCl</td>
<td>0</td>
<td>Na⁺</td>
<td>0.2</td>
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<tr>
<td>KCl</td>
<td>0.2013</td>
<td>K⁺</td>
<td>0.0036</td>
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<tr>
<td>MgCl₂.6H₂O</td>
<td>1.5491</td>
<td>Mg²⁺</td>
<td>0.0190</td>
</tr>
<tr>
<td>MgSO₄.2H₂O</td>
<td>0.5438</td>
<td>Ca²⁺</td>
<td>0.0087</td>
</tr>
<tr>
<td>CaCl₂.2H₂O</td>
<td>0</td>
<td>Cl⁻</td>
<td>0.065</td>
</tr>
<tr>
<td>CaSO₄.2H₂O</td>
<td>1.5842</td>
<td>SO₄²⁻</td>
<td>0.1</td>
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<tr>
<td>SrCl₂.6H₂O</td>
<td>0.0216</td>
<td>F⁻</td>
<td>0.0003</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>12.843</td>
<td>HCO₃⁻</td>
<td>0.0008</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>0.0748</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaF</td>
<td>0.0092</td>
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The bentonite water should correspond to the composition of sodium bentonite Volclay KWK 20-80 of a density of 1600 kg.m⁻³.

The equipment for measuring hydrogen generation rate for first and second type of corrosion experiments in anaerobic box is shown in Fig. 1.

Fig. 1 The device for hydrogen evolution measurements. 1 – Heater, 2 – Constant pressure chamber, 3 – Sample, 4 – Gas sampling valve, 5 – Temperature regulator, 6 – Data acquisition equipment, 7 – Volume change detector, 8 – Source of constant pressure, 9 – Temperature sensor

This device enables to measure hydrogen evolution continuously at different temperatures and at a constant pressure in water. The source of pressure is heavy piston, moving in mutually interconnected pressurized cylindrical vessels with a rolling membrane (Bruha and Pelech, 1989) (Bruha and Pelech, 1989). The measurement of volume is based on the detection of the piston position, which depends on the medium volume.

The device developed in this project for measuring hydrogen evolution rate for the third type of experiment with cylindrical carbon steel sample is shown in Fig. 2. It uses the same principle of measuring hydrogen generation rate from the volume change with LVDT Displacement Transducer as described above.
Fig. 2 Corrosion chamber for cylindrical samples 1 – chamber case, 2 – chamber body, 3 – cover, 4 – nut, 5 – inlet/outlet, 6 – inlet/outlet, 7 – needle valve, 8 – well for temperature sensor, 9 – well for temperature sensor, 10 – heater, 11 – temperature sensor, 12 – sealing, 13 – sealing, 14 – solution or bentonite, 15 – filtration textile, 16 – sample.

The experiments were conducted in anaerobic box (MBraun, Germany) filled with argon with concentration of oxygen below 0.1 ppm (Fig. 3).
Combined platinum electrode ORC 103–BAZ (Theta ‘90, Czech Republic, platinum disc of diameter 4 mm) was used to measure Eh in the system with steel plates (measuring period 1 day). The same platinum electrode and additional XCL 101 XB2 platinum electrode (Gryf HB, Czech Republic, platinum disc of diameter 2 mm) were used for measuring the redox potential in the corrosion system with iron powder. For measuring pH HC 113 electrode (Theta ‘90, Czech Republic) was used and in the system with the iron powder also pH PCL 321 XB2 electrode (Gryf HB, Czech Republic). Combined gold electrode ORC 103 (Theta ‘90, Czech Republic, gold disc of diameter 4 mm) and combined gold electrode ORC 103 XB2 (Gryf HB, Czech Republic, gold disc of diameter 4 mm) were used for measuring Eh of long-term experiments (i.e. 1-year experiments).

The experiments were carried out at various temperatures controlled by a TDC 2 Temperature Controller (Gamry Instruments Inc, USA) with a Series 988 PID control unit (Watlow Controls, USA) or temperature controller E5CSV (Omron, Japan).

Corrosion products on the carbon steel plates after the experiments were measured by Raman spectrometer LabRam (Horiba - Jobin Yvon, France) with two lasers (He – Ne and Ar), by X-ray diffraction Philips-Xpert PRO (PANalytical, Netherlands) and by ESCA Probe P (Omikron Nanotechnology, Germany) in CAE mode (Constant Analyser Energy).

Another device was developed for experiments which involved compacted bentonite in contact with steel cylinders. In addition to measuring changes of hydrogen volume using LVTD Displacement Transducer Sensor, this specific corrosion chamber enables to measure swelling pressure and pressure induced by hydrogen evolution. The samples of compacted bentonite, prepared using compression testing machine, were saturated under high pressure using Haskel Pump, Model MS-21.

2.2 HYDROGEN GENERATION

2.2.1 Long-term corrosion experiment

The long-term experiments with cylindrical carbon steel samples under anaerobic condition were performed in the corrosion chamber shown in Fig. 2. Temperature of the samples was 80 °C during the whole experiments. Hydrogen accumulation curve for one year experiment with synthetic bentonite pore water is reported in Fig. 4. It can be seen that hydrogen accumulation curve increases first sharply and then relatively linearly. Corresponding curve of hydrogen evolution rate calculated from regression curve of hydrogen accumulation is given in Fig. 5. It can be observed that after the 100 days of the experiment the hydrogen evolution rate is below 1 mol.m⁻².yr⁻¹. This decrease of hydrogen evolution rate is caused by creation of protective corrosion product layer.

The carbon steel sample after dismantling of the corrosion chamber is shown in Fig. 6. The analysis of the corrosion product layer by X-ray diffraction proved magnetite. It can be seen in Fig. 7 that the carbon steel sample is partly covered by a thin white layer (probably calcium sulphate), which was over the magnetite layer. The amount of this white layer was under detection limit of X-ray diffraction and Raman spectroscopy. The corrosion rate obtained from weight loss measurement is 5.58 µm.yr⁻¹.

The results of measuring redox potential and pH with various types of electrodes are given in Fig. 8. It can be observed relatively large range of values of redox potential, though the system remained globally in reducing conditions. A discussion on variations in redox potential is given in section 1.2.2 related to short-term experiments.
Fig. 4 Hydrogen accumulation curve for 1 year experiment at 80 °C

Fig. 5 Hydrogen evolution rate
Fig. 6 Carbon steel sample after 1 year experiment in synthetic bentonite pore water at 80 °C
Fig. 7 Magnetite under the white layer

Fig. 8 : Results of measuring Eh and pH of the solution

Hydrogen accumulation curve for second long-term experiment (still in progress) is shown in Fig. 9. The character of this curve is similar with that of the first long-term experiment as it can be seen from comparison of first and second long-term experiment in Fig. 10.
Fig. 9 Hydrogen accumulation curve for long-term experiment at 80 °C

Fig. 10 Comparison of hydrogen accumulation curves of long-term experiments
2.2.2 Short-term corrosion experiments

**Experiments with cylindrical carbon steel samples**

Short-term experiments under various temperatures have been carried out with cylindrical carbon steel samples in synthetic bentonite pore water using the device shown in Fig. 2. Hydrogen accumulation curves of these experiments are in Fig. 11. Absolute values of hydrogen volumes are very low in comparison with long-term experiments at same time. The reason why there is this difference on the same material is not obvious at present time. It may have been caused by inhomogeneities in the material (same standard EN 10204/3.1) from which the samples were made or leaking of hydrogen from the corrosion chamber in the short-term experiments.

![Hydrogen accumulation curves of short-term experiments converted to 25 °C](image)

The same type of experiments was also carried out with solid bentonite, either compacted or not. The corrosion rate of carbon steel in contact with solid bentonite is almost one order of magnitude higher than the corrosion rate of carbon steel in bentonite water solution. In all the experiments, the average corrosion rate of carbon steel after 30 day experiment was 30 μm/year (hydrogen evolution rate of 6 mol m⁻² yr⁻¹, approximately) contrary to 2 to 5 μm/year in solution. This finding can be explained by the nature of corrosion layers formed on the surface of samples caused by so called “pumping” effect of bentonite. Iron species are sorbed on bentonite and thus do not contribute to the formation of an adherent corrosion layer. This might also be explained by other reasons such as high concentration of iron (III) in bentonite. The first hypothesis is supported by a fast transport of iron species to bentonite as can be seen in Fig. 12.
Fig. 12 Compacted bentonite after 30 days of contact with carbon steel

Experiments with carbon steel plates

The result of hydrogen evolution from experiments conducted in an anaerobic box with 10 or 1 carbon steel plates in 2 l of synthetic bentonite pore water are shown in Fig. 13, Fig. 14, Fig. 15 and Fig. 16. In the case of 10 samples the hydrogen evolution rate decrease below 1 mol.m$^{-2}$.yr$^{-1}$ (Fig. 16). Contrary to these results hydrogen evolution rate for one sample increased after some time of corrosion (Fig. 14). The reasons for this increase in hydrogen evolution rate could be associated to the decrease in pH (see Fig. 19) but have not been fully clarified yet.

Fig. 13 Hydrogen evolution curves from experiments with 1 carbon steel plate
Fig. 14 Hydrogen evolution rates from experiments with 1 carbon steel plate

Fig. 15 Hydrogen evolution curves from experiments with 10 carbon steel plates
These results can be explained by the formation and dissolution of protective corrosion product layers on the surface of carbon steel. The stability of corrosion layers depends on the evolution of the conditions in the solution, primarily pH and Eh. But both pH and Eh are strongly affected by corrosion process itself. Different conditions were reached with 10 samples corroded in 2 l of water (Fig. 17, Fig. 18) and with 1 sample corroded in 2 l of water (Fig. 19, Fig. 20). With 10 samples Eh initially slightly above 0 mV very quickly decreases to low values immediately after immersion of samples in the solution. This indicates that remained oxygen quickly reacted with iron to form corrosion products, such as ferrous hydroxide or magnetite. Then, Eh increased with the formation of corrosion products with ferric ions, such as maghemite or hematite. pH decreases, but we cannot explain this decrease at present time. It can be supposed that under these conditions a rather stable corrosion product layer was formed which strongly limit further corrosion and hydrogen rate evolution.

Contrary, after immersion of 1 sample of carbon steel in 2 l of bentonite water solution, Eh decrease was much lower (Fig. 19). It indicates that iron from carbon steel did not react with oxygen efficiently (Eh of -70 to -250 mV) enough to form stable protective corrosion product layers in comparison with the experiment with 10 plates (Eh of -200 to -350 mV). The least stable was the corrosion product layer formed under corrosion at 40 °C.

Fig. 16 Hydrogen evolution rates from experiments with 10 carbon steel plates
Fig. 17: The change of Eh in experiments with 10 samples of carbon steel in bentonite water

Fig. 18: Change of pH during corrosion of 10 samples in 2 l of bentonite water
The nature of corrosion products layers was analysed using X-ray diffraction and Raman spectroscopy. Corrosion product layers formed on the surfaces of the samples from experiments with one carbon steel plate conducted at 40 °C and 50 °C were under the detection limit of Raman spectroscopy and X-ray diffraction. This confirms that the thickness of these layers was very thin and can explain why the hydrogen evolution rates of some samples started to increase after some time.
The corrosion product layer of the sample from the experiments carried out at 60 °C and 70 °C was also under the detection limit of X-ray diffraction but by Raman spectroscopy magnetite/maghemite (band 676 cm$^{-1}$), maghemite (1430 cm$^{-1}$) and hematite (band 220 cm$^{-1}$) were detected (Fig. 21 and Fig. 22).

Fig. 21: Raman spectrum from a carbon steel plate placed at 60 °C.

Fig. 22: Raman spectrum from a carbon steel plate placed at 70 °C.
Interesting results that emerged from our experiments were achieved by analysing the elementary composition of the corrosion layers by ESCA. A relatively large number of elements were detected, but with very low percentages, so that only the 3 most important elements: C, O, and Fe are shown in Table 4 and Table 5. Table 4 shows the results after etching (evaporation) a very thin surface layer (thickness nm) by an electron beam. It can be seen that after removing the first layer affected by atmospheric corrosion, the percentage of iron on the surface of a non-corroded sample is much higher than on the surfaces of corroded samples. The oxygen content in surface layers increases with the corrosion temperature. Therefore we can say that this method provided evidence that an adhering corrosion layer of non-negligible thickness was formed on the surface of carbon steel during anaerobic corrosion at 60 and 70 ºC, protecting carbon steel against further fast corrosion. The oxygen content in the surface layers of samples corroded at 60 ºC and 70 ºC, is, however, higher than the stoichiometric ratio of Fe/O in magnetite or maghemite so that the results suggest that the composition of passive corrosion products layers is not only formed by an inner layer of magnetite and outer layer of maghemite as proposed in previous papers (Kruger, 1989; Lu and Macdonald, 2008).

Table 4: Corrosion layer composition measured at different temperatures. Blank means a sample without a corrosion layer.

<table>
<thead>
<tr>
<th>sample/temperature, °C</th>
<th>Blank</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 1s</td>
<td>49.37</td>
<td>64.33</td>
<td>37.4</td>
<td>29.2</td>
<td>50.27</td>
</tr>
<tr>
<td>O 1s</td>
<td>34.72</td>
<td>23.07</td>
<td>44.77</td>
<td>47.7</td>
<td>35.92</td>
</tr>
<tr>
<td>Fe 2p</td>
<td>9.89</td>
<td>1.47</td>
<td>4.21</td>
<td>5.33</td>
<td>2.75</td>
</tr>
</tbody>
</table>

Table 5: Corrosion layer composition after evaporating (etching) a thin surface layer by an electron beam. Blank is a sample without a corrosion layer.

<table>
<thead>
<tr>
<th>etching</th>
<th>sample/temperature, °C</th>
<th>Blank</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 1s</td>
<td>7.44</td>
<td>53.2</td>
<td>19.74</td>
<td>4.89</td>
<td>12.95</td>
<td></td>
</tr>
<tr>
<td>O 1s</td>
<td>6.41</td>
<td>19.47</td>
<td>33.56</td>
<td>52.67</td>
<td>50.10</td>
<td></td>
</tr>
<tr>
<td>Fe 2p</td>
<td>86.15</td>
<td>9.77</td>
<td>26.04</td>
<td>21.14</td>
<td>14.57</td>
<td></td>
</tr>
</tbody>
</table>

The results confirm that protective corrosion product layers are formed in bentonite pore water solutions on the surface of carbon steel samples, but their stability depends strongly on the conditions of corrosion, primarily temperature, Eh and presumably pH.

Globally, regarding the effect of temperature, one can say on the basis of the whole set of results obtained that at the very beginning of the corrosion process, the higher the temperature is, the higher the initial hydrogen generation rate. Then, the temperature effect depends on the nature and stability of the corrosion layer. Thus, WP2 experiments tend to indicate that hydrogen generation rate is not proportionally related to temperature (in the tested range), except at the very beginning of the corrosion process.
Experiments with iron powder

In many research works focusing mainly on modelling of the effect of canister material corrosion on the evolution of the conditions in a repository, iron powder is used instead of carbon steel ((de Combarieu et al., 2007; Lantenois et al., 2005; Osacký et al., 2010; Perronnet et al., 2007)). For comparison sake and also to accelerate corrosion reactions, particularly under low temperatures, iron powder with large surface was used in some of the experiments instead of carbon steel samples.

The experiments with iron powder were also conducted in the anaerobic box. Hydrogen accumulation curves for iron powder corroded at 70 °C in synthetic bentonite pore water are shown in Fig. 23 (there are curves for experiment with 30 g of iron powder, 30 g of iron powder with 10 g of solid bentonite Volclay KWK 20-80 in a permeable bag and 5 g of iron powder in 2 L of synthetic bentonite pore water). It can be seen that contrary to the results with carbon steel plates hydrogen accumulation curves started to increase only after several days and the rate of this increase was linear. It could suggest that an initial protective iron oxide layer was dissolved during the first 10 days under these conditions and only after this time active corrosion of iron started.

Fig. 23 Hydrogen accumulation curves per 1 m$^2$ of iron powder surface

In Fig. 23 is possibly seen that hydrogen evolution per m$^2$ is higher for experiments with 30 g of iron powder. It can be explained by comparing the hydrogen accumulation curves with corresponding redox potential (Fig. 24). It is possible that for experiment with 5 g of iron powder the system is in passive Eh/pH-region (Fe$_3$O$_4$) while for experiments with 30 g of iron it is in active corrosion state, which is below the passive region.

The change of pH during the experiment wasn’t observed (Fig. 25). Hydrogen evolution rate have linear character for all experiments after approx. ten days. The values are: 0.8 mol.m$^{-2}$.yr$^{-1}$ (30 g of Fe powder), 1.2 mol.m$^{-2}$.yr$^{-1}$ (30 g of Fe powder and 10 g of bentonite Volclay), 0.28 mol.m$^{-2}$.yr$^{-1}$ (5 g of Fe powder).
Corrosion products were analysed using X-ray diffraction (Fig. 26, Fig. 27, Fig. 28) and Raman spectroscopy. Both methods prove magnetite for all three experiments with iron powder and goethite for experiment with bentonite Volclay in the system.

Regarding the effect of bentonite in the solid form (present in a permeable bag) on the rate of corrosion, it can be seen (Fig. 23) that the character of the hydrogen accumulation curve is practically the same as that obtained without solid bentonite. The rate of hydrogen evolution is little higher (1.2 to 0.8 molm\(^{-2}\)yr\(^{-1}\)), but it is difficult to conclude on the basis of this comparison that the presence of solid bentonite will accelerate hydrogen generation rate. However, it is worth remembering that in this case bentonite is not in contact with the steel sample.

Comparing these experiments carried out with powders in synthetic bentonite pore water with those carried out with carbon steel plates, the stronger decrease in Eh (around -400 to -500 mV) obtained with powders yields to a less inhibited corrosion (higher hydrogen generation rates per m\(^2\)) than that observed for the lower Eh decrease (around -200 mV) with carbon steel plates. An important parameter is thus the ratio of surface of metals to the volume of water, as it primarily affects the oxidation potential of water in contact with metals: while the (slight) presence of oxygen impacts hydrogen generation rates at the beginning of corrosion until a sufficiently protecting layer is formed, strongly reducing environment can also favour hydrogen generation, possibly as the stable corrosion product layer cannot be reproduced after dissolution.

![Fig. 24 Redox potential for experiments with iron powder](image-url)
Fig. 25 Comparison of pH in systems with iron powder

<table>
<thead>
<tr>
<th>Ref. Code</th>
<th>Score</th>
<th>Compound Name</th>
<th>Mineral Name</th>
<th>Chemical Formula</th>
<th>SemiQuant [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>03-065-4899</td>
<td>55</td>
<td>Iron</td>
<td></td>
<td>Fe</td>
<td>55</td>
</tr>
<tr>
<td>03-065-3107</td>
<td>71</td>
<td>Iron Oxide</td>
<td></td>
<td>Fe$_3$O$_4$</td>
<td>45</td>
</tr>
</tbody>
</table>

Fig. 26 X ray diffraction spectrum for experiment with 30 g of Fe powder
Ref. Code   | Score | Compound Name     | Mineral Name | Chemical Formula | SemiQuant [%] \\
-------------|-------|-------------------|--------------|------------------|---------------
01-076-1849 | 81    | Iron diiron(III) oxide | Magnetite    | Fe$_3$O$_4$      | 50            \\
00-002-0273 | 24    | Goethite          | Goethite     | FeO(OH)          | 10            \\
00-006-0696 | 46    | ferrite           | Iron, syn    | Fe               | 40            \\

Fig. 27 X ray diffraction spectrum for experiment with 30 g of Fe powder and bentonite Volclay

Ref. Code   | Score | Compound Name     | Mineral Name | Chemical Formula | SemiQuant [%] \\
-------------|-------|-------------------|--------------|------------------|---------------
01-089-3854 | 71    | Iron diiron(III) oxide | Magnetite, syn | Fe$_3$O$_4$      | 8             \\
03-065-4899 | 67    | Iron              | Fe           |                  | 92            \\

Fig. 28 X ray diffraction spectrum for experiment with 5 g of Fe powder
3 IRSN Experiments

3.1 INTRODUCTION

Within geological disposal facilities, depending on their design, iron or carbon steel components (radioactive waste containers) may be exposed simultaneously to radiation and to water when their environment (host-rock, bentonite...) will be re-saturated. In such conditions, corrosion processes and water decomposition under radiation will generate gases, mainly hydrogen. Actually, radiolysis of water will occur and produce both radicals and molecular products which could influence corrosion processes and the generation of hydrogen (production/depletion). The understanding of the global system behaviour is a prerequisite to assess the gas production rate, which is one of the input data for modelling hydrogen transport in a repository. The aim of this study is to examine the influence of γ irradiation on hydrogen generation by iron corrosion. After a brief description of the state of the art, the experiments carried out and the results obtained are presented and discussed. Main conclusions are drawn on this basis, and needs for complementary studies are identified.

3.2 STATE OF THE ART

When exposed to radiation (α, β, γ, recoil nuclei), water molecules are exited and ionized, and water is decomposed as follows:

\[
\text{H}_2\text{O} \rightarrow \text{OH}^\circ, \text{e}^-_{\text{aq}}, \text{H}^\circ, \text{HO}_2^\circ, \text{H}_2, \text{H}_2\text{O}_2, \text{H}^+
\]

where species noted \(^\circ\) are radicals and \(\text{e}^-_{\text{aq}}\) corresponds to a solvated electron.

Once generated, the primary products undergo further chemical reactions with each other (Ershov and Gordeev, 2008), with water molecules and with chemical species present in solution. The steady-state concentration of radiolysis products depends on their radiolysis production rate and recombination reactions (Yakabuskie et al., 2010).

In a completely closed single-phase situation, almost never encountered in practice, the irradiation of de-aerated water produces a little effect, and low steady state concentrations of radiolysis products are obtained according to Allen chain (Table 6), the kinetic constants of the two recombination reactions being in the same range.

**Table 6: Allen chain**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Kinetic Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{OH}^\circ + \text{H}_2 \rightarrow \text{H}^\circ + \text{H}_2\text{O}) (R1)</td>
<td>(k_1 = 4.2 \times 10^7 \text{L}^{-1}\text{mol.s}^{-1})</td>
</tr>
<tr>
<td>(\text{H}^\circ + \text{H}_2\text{O}_2 \rightarrow \text{OH}^\circ + \text{H}_2\text{O}) (R2)</td>
<td>(k_2 = 3.7 \times 10^7 \text{L}^{-1}\text{mol.s}^{-1})</td>
</tr>
</tbody>
</table>

If water contains few ppm of dissolved oxygen, the reducing species \(\text{e}^-_{\text{aq}}, \text{H}^\circ\), are rapidly (high kinetics constants) converted to \(\text{O}_2^\cdot\) and \(\text{HO}_2^\circ\) respectively:

\[
\begin{align*}
\text{O}_2 + \text{e}^-_{\text{aq}} &\rightarrow \text{O}_2^\cdot \quad (R3) \\
\text{O}_2 + \text{H}^\circ &\rightarrow \text{HO}_2^\circ \quad (R4)
\end{align*}
\]

\(k_3 = 1.9 \times 10^{10} \text{mol}^{-1}\text{l.s}^{-1}\)

\(k_4 = 2.1 \times 10^{10} \text{mol}^{-1}\text{l.s}^{-1}\)

Therefore, Allen’s chain is disrupted and water decomposition occurs. For example, at pH 6, for a dose rate of 25Gy/s (γ Rays), the steady-state concentration of H₂ and H₂O₂ in aerated solutions...
reached respectively $2.6 \times 10^{-5}$ mol/l and $9 \times 10^{-5}$ mol/l, while it remains below the detection limit ($3 \times 10^{-6}$ mol/l) in de-aerated solutions (Joseph et al., 2008).

In the same way, if gases produced in solution are removed from the system, aqueous hydrogen concentration decreases and water decomposition of water is also observed because of the disruption of Allen chain.

Finally, radiolytical species can react with chemical species present in solution, and modify their concentrations and their speciation (Cai et al., 2001).

Dissolved iron issuing from corrosion reacts with radicals (Bouniol, 2010, Garrido-Ramirez et al., 2010):

$$\text{Fe}^{2+} + \text{OH}^* \rightarrow \text{Fe}^{3+} + \text{OH}^- \quad (R5) \quad k_5 = 3.2 \times 10^8 \text{ mol}^{-1}.\text{l.s}^{-1}$$

$$\text{Fe}^{3+} + e_{aq}^- \rightarrow \text{Fe}^{2+} \quad (R6) \quad k_6 = 6 \times 10^{10} \text{ mol}^{-1}.\text{l.s}^{-1}$$

$$\text{Fe}^{2+} + \text{HO}_2^* \rightarrow \text{Fe}^{3+} + \text{HO}_2^- \quad (R7) \quad k_7 = 1.3 \times 10^6 \text{ mol}^{-1}.\text{l.s}^{-1}$$

Ferrous ions will also undergo a homogeneous reaction with $\text{H}_2\text{O}_2$ in the Fenton reaction (Wu et al., 2012):

$$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{OH}^* \quad (R8) \quad k_8 = 76 \text{ L}^{-1}\text{mol.s}^{-1}$$

As soon as species produced by water radiolysis can react with other components present in the system (solid phase, aqueous component), the steady-state balance between radiolytic species is disrupted, their concentrations evolve and the production of hydrogen is modified.

Water radiolysis produces both oxidizing ($\text{OH}^*$, $\text{H}_2\text{O}_2^*$) and reducing ($\text{H}_2$, $e_{aq}^-$) species, which can modify the redox conditions and therefore influence iron corrosion processes either directly or through modification of the structure of corrosion layer (Burns et al., 1983).

Several authors have put in evidence enhanced corrosion of different metals such as zircaloy under charged particle radiations (Burns et al., 1983, Ishigure et al., 1980, Lapuerta et al., 2005, Lillard et al., 2000). But gamma radiations seem to have a little effect on materials properties.

Marsh and Taylor (1988) have compared steel corrosion in synthetic seawater under and without irradiation. Unirradiated experiments have been conducted for periods up to 5000 h (200 days); the general corrosion rate obtained settled at 6 µm/y and no localized attack was developed. The irradiated tests, conducted for periods up to 9600 h (400 days), showed appreciable acceleration in the rate of corrosion with the weight loss measurements indicating corrosion rates exceeding 100 µm/y in some tests at the highest dose rate ($1.5 \times 10^3$ Gy/h). But, visual inspection showed that much of the corrosion at all three dose rates ($3$, $35$ and $1.5 \times 10^3$ Gy/h) had occurred as patches of attack on the edges of the specimens, which suggests that it may be associated with some metallurgical inhomogeneity in the steel. In some cases these areas had penetrated up to 0.5 mm and the variability in the number and size of these local sites accounts for the large scatter in the weight loss data.

Fujita et al. (2000, 2001) have measured a corrosion rate in pure de-aerated water under a dose rate of $5.5 \times 10^2\text{ Gy/h}$ for 300, 600 and 900 h six times larger as that under a non-irradiated condition. An other experimental study (Marsh and Taylor, 1988) on the corrosion of carbon steel in presence and absence of radiation (dose rate up to $10^3\text{ Gy/h}$) was carried out in synthetic granitic waters ($\text{pH} = 9.4$). Without irradiation, the rate of general corrosion was less than 0.1 µm/y. In the same environment, with a maximum $\gamma$ dose rate of $10^3\text{ Gy/h}$, the general corrosion rate was fairly constant at 3 µm/y at least, up to 5236 h (~218 days corresponding to the duration of the experiment). As on unirradiated samples, no localized corrosion was observed.
Smart et al. (2008) also found that radiation (11 Gy/h, 300 Gy/h) enhanced the corrosion rates of carbon steel wires in contact with 2 synthetic groundwaters (equilibrated with granite and with bentonite, anaerobic conditions). The corrosion rate value estimated on the basis of hydrogen release is closed to values obtained by Marsh and Taylor (1988), 3 µm/y, compared to less than 0.1 µm/y without radiation. No localized attack was observed. Smart et al. (2008) also mentioned a more pronounced enhancement of the corrosion rate under radiation for “granitic water” than for “bentonite water”. A 30 fold increase was observed in granitic water while for bentonite water (higher ionic strength, higher initial pH value), the radiation-induced enhancement was 10-20 times. Nevertheless, the authors observed that hydrogen generation rate and thus the corrosion rate decrease over time, the differences in corrosion rates without and under radiation becoming insignificant after a 83 days period.

The chemical nature and morphology of surface oxide films produced by iron corrosion are important parameters in controlling corrosion rates. Ionizing radiation may affect the semi-conducting properties of these passive films (Mucka and Mizik, 1991) by altering the number and type of charge carriers. In most cases γ irradiated oxides changed their properties such as the crystalline size and their lattice parameter. Wang and Xin (1999) have observed that the irradiation of β-FeOOH have induced an evolution towards α-FeOOH in the initial stage of the irradiation process. With the γ-irradiation continued, α-FeOOH was slowly reduced to Fe$_3$O$_4$. After the γ-irradiation with a dose of 64.3 kGy, all the β-FeOOH and α-FeOOH disappeared and the product was a single phase of magnetite (Fe$_3$O$_4$).

Daub et al. (2011) have studied the effect of γ-radiation on the kinetics of carbon steel corrosion in alkaline conditions (two pH values) at high temperature 150°C. They concluded that irradiation enhances surface oxide formation with the type of oxide formed dependant on the solution pH. For experiments at 150 °C and pH = 10.6, the surface oxide (mixture of Fe$_3$O$_4$ and γ-Fe$_2$O$_3$) on carbon steel after γ-irradiation was non-porous and uniform, and no localized corrosion was observed. In contrast, at 150 °C and neutral pH, metal dissolution is significant and the surface oxide film is very porous. Raman spectra show that this oxide film is also composed of a mixture of Fe$_3$O$_4$ and γ- Fe$_2$O$_3$. Previous studies (Zhang et al., 2007, Daub et al., 2008) found that the oxide formed in absence of radiation is mainly Fe$_3$O$_4$, while the oxide formed under irradiation has a mixed Fe$_3$O$_4$/γ- Fe$_2$O$_3$ structure. They have also demonstrated that the results obtained by irradiation are well mimicked by adding H$_2$O$_2$ to the solution.

Thus, in many cases, the main corrosion product of carbon steel in contact with deaerated water is magnetite, Fe$_3$O$_4$, but there was some evidence of higher oxidation state oxyhydroxides (Fe$_3$O$_3$, FeOOH) under high dose rate (Xu et al., 2008, Daub et al., 2009). Smart et al. (2008) mentioned that the corrosion product formed under high dose rate (300 Gy/h) has a different color to the specimen obtained at 0 and 11 Gy/h. (Fujita et al., 2000) have observed through X-Ray diffraction analysis a preferential dissolution of a specific (110) plane, which potentially triggers an occurrence of the pitting corrosion and an incipient crack.

As a conclusion, studies devoted to corrosion under radiation tend to indicate that the corrosion of carbon steel in reducing conditions is enhanced under irradiation. But uncertainties still remain about the processes as well as the factor of enhancement, which may range between about 1 and 30. For example, no unanimity was obtained regarding the state of the surface of carbon steel corroded under irradiation: is it generalized or localized corrosion? Authors have observed the formation at the interface steel/solution of magnetite together with oxy-hydroxides. It would worth examining the influence of the structure of the corrosion layer on the corrosion rate. Besides, no specific data were reported on the redox potential evolution during experiments, while this could help understanding the processes involved. At last, the behaviour of hydrogen (production/consumption) as well as the influence of dissolved species (carbonate, chloride...) on this behaviour and on corrosion under
radiation has not been addressed. More generally, there is a need for a better understanding of corrosion and hydrogen production/consumption processes under radiation, so as to improve the assessment of intensity and duration of radiation effects on hydrogen generation.

### 3.3 EXPERIMENTAL METHOD

Usually, corrosion rates are determined by pressure measurement or loss of mass by steel after corrosion. According to the objectives of FORGE-WP 2, we needed to monitor hydrogen generation during all the duration of the planned experiments. The choice was made to use an “open” (flushed) experimental cell together with Gas Chromatography (GC) as this technique provides continuous and fine measurements of hydrogen fluxes. This technique also gives the opportunity to shift the apparatus from the irradiation facility in order to prevent any damage induced by irradiation of the GC apparatus.

![Fig. 29: Gas Chromatography apparatus](image)

In first experiments, we used UJV device (Fig. 2) in which carbon steel is present as a compact tube. In spite of the low detection limit of GC, the surface offered to corrosion processes is too low to induce enough hydrogen production for GC measurement. Moreover, the air tightness of the cell is ensured by O-rings (neoprene) which are damaged by irradiation (Croonenborghs et al., 2007) and are not able to prevent from any leakage.

After different tests (see Stammose and Vokal, 2012b), a new experimental cell (stainless steel) was developed without any organic component. Different tests have shown the absence of leakage. This cell (Fig. 30) of 430 ml (internal volume) is equipped with 3 tubes which allow a bubbling of the solution (1) in order to minimize the amount of solubilized gases, (2) to control both pressure and temperature in the cell, and (3) the connection of gaseous atmosphere of the cell to GC in order to monitor gas production. Hydrogen flow rate is calculated assuming that all hydrogen produced is in the gaseous phase (Henry’s law).
A scheme of the whole experimental setup, developed in 2010-2011, is presented in Fig. 31.

Irradiation experiments were performed at IRSN (Saclay, France) in IRMA (IRradiation MAtériaux) facility (Fig. 32). This facility (24 m³) is devoted to the study of the radiation-matter interactions and more specifically to the behaviour of materials and devices under γ-irradiation.
Fig. 32: IRMA facility

Four cylindrical sealed sources ($^{60}$Co) with different activities are available for irradiation (see values in Table 7). Their diameters are 10 mm and their lengths vary between 229 and 452 mm. The dose rate available ranges between 5 μGy/h and 15 kGy/h.

**Table 7 Characteristics of $^{60}$Co sources**

<table>
<thead>
<tr>
<th>Source Reference</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activity (TBq)</td>
<td>89.57</td>
<td>86.51</td>
<td>161.97</td>
<td>163.80</td>
</tr>
</tbody>
</table>

The conditions of irradiation (number and position of the sources, duration of irradiation...) were chosen in order to have a homogeneous distribution of energy in the cell.

The experiment sequences are described in Fig. 33. Step 1 corresponds to a pure corrosion phase. This step is achieved as soon as the hydrogen production is constant. Then irradiation is applied (Step 2). The optimal duration corresponds to the time necessary to obtain a plateau (like in Step 1). When irradiation is stopped, ideally hydrogen release is measured until to obtain a plateau again (Step 3). However, in some cases, it was necessary to stop irradiation or the experiment before to reach these plateaus because of the availability of IRMA.

Fig. 33: Sequence of an experiment
At the end of the experiment, the cell is dismantled and both solution (pH, redox potential, conductivity) and solid (Raman spectroscopy) are analysed.

The quantification of H$_2$O$_2$ according to Ghormley method (Joseph et al., 2008) is not applicable for solutions containing soluble iron species. Thus, H$_2$O$_2$ concentration was estimated for one experiment with specific indicators (Merck).

Four experiments were performed, which parameters are gathered in Table 8.

**Table 8: Experimental conditions for experiments 1 to 4**

<table>
<thead>
<tr>
<th>Experiments</th>
<th>Mass of Fe(0) (g)</th>
<th>Granulometry (µm)</th>
<th>Dose rate (Gy/h)</th>
<th>Specific area (m$^2$/g) *</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>&lt;210</td>
<td>100</td>
<td>0.0036</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>&lt;210</td>
<td>50</td>
<td>0.0036</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>&lt;10</td>
<td>11</td>
<td>0.205</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>&lt;10</td>
<td>50</td>
<td>0.205</td>
</tr>
</tbody>
</table>

*Specific area was determined by BET measurements for granulometry less than 10 µm. For Φ < 210µm, the surface, too low to be measured by BET, was calculated assuming that particles are spherical. This value is probably underestimated, the particles porosity being neglected.

### 3.4 RESULTS

For **experiment 1** (100 Gy/h), the hydrogen generation rate (in mol/min) as a function of time is plotted in Fig. 34, together with the temperature variations in the room. The temperature in the cell was not measured; however it can be assumed that this temperature was close to 25°C during all the experiment. The pressure in the cell was monitored and was close to atmospheric pressure during all the experiment (no overpressure).
The “pure” corrosion phase (without irradiation) lasted only 1.5 days (availability of IRMA facility). Nevertheless, a plateau (corresponding to a pseudo-steady state corrosion rate) seemed obtained. As soon as irradiation began, H₂ production increased sharply due to water radiolysis, until to reach a new plateau corresponding to the sum of hydrogen produced by corrosion with that produced by water radiolysis. The plateau lasted 16 days and was followed by an increase of hydrogen production rate which continued during all the irradiation phase. When irradiation was stopped, H₂ generation rate decreased (same amplitude of decrease than the amplitude of increase observed at the beginning of irradiation due to water radiolysis), and then increased again without reaching a plateau (1 week).

The same global evolution of H₂ generation versus time was obtained for experiment 2 (dose rate = 50 Gy/h) presented in Fig. 35. Corrosion occurred during 8 days before irradiation and a plateau was obtained. After the beginning of irradiation, a short plateau (1 day) was observed, followed by a strong increase which lasted 6 days and then a weaker increase in hydrogen generation. Like in the previous experiment, when irradiation was stopped, the hydrogen generation rate was still increasing.
The evolution of hydrogen production rate measured for experiment 3 (dose rate = 11 Gy/h) was different from that observed in the previous experiments, as shown in Fig. 36.
During the “pure” corrosion step (close to 10 days), H₂ rate was around $1.7 \times 10^{-7} \pm 5 \times 10^{-8}$ mol/min. During all the experiment, temperature was in the same range than the previous experiments (20-30°C). However, iron particles had a lower granulometry (<10µm) than in experiments 1 and 2. Consequently, the surface offered to corrosion processes was much higher (x 60) and the production rate of hydrogen by corrosion was higher. Three irradiation’s phases were applied during this experiment, lasting respectively 6, 5 and 27 days. During the third irradiation phase, a problem with gas chromatograph occurred and H₂ was not measured continuously. No increase of hydrogen production was observed for the two first irradiation sequences: hydrogen production rate was constant during the first 25 days of the experiment. Then, though irradiation was stopped, hydrogen rate increased until 60 days of experiment. When the third irradiation was stopped (81 days), H₂ generation rate decreased without to reach a plateau (10 days).

In experiment 4, Fe particles size was <10 µm and the dose rate was 50 Gy/h in order to compare to the variations obtained in experiment 2 ($\Phi < 210$ µm). The mixture Fe (0)/H₂O was introduced in the experimental cell and the closed cell was stored in a glove box during 90 days, so as to have a long “pure corrosion” step. Hydrogen produced during this phase remained inside the cell and the pressure increased. After 90 days, the cell was connected to the gas chromatography apparatus and the degassing of the system by He 4.5 was applied. Four irradiation sequences were then applied to this cell. The variations in hydrogen generation are plotted in Fig. 37.

![Fig. 37: Evolution of hydrogen production rate – Experiment 4 – Dose rate = 50Gy/h – Total dose = 34.2 k Gy](image)

After 90 days, H₂ production rate varied between $9 \times 10^{-7}$ and $1.8 \times 10^{-6}$ mol/min. In spite of the 3 months of contact, no clear steady state was obtained. An important variation was observed for the first measurements because of time necessary to reach equilibrium between aqueous and gaseous H₂. Actually, this first step of measuring corrosion without irradiation have had to be short (lasting 5 days) due to constraints regarding the availability of IRMA facility.
For each irradiation phase, the same variation was observed: a decrease of the production rate when irradiation was applied and an increase when irradiation was stopped. This is the opposite behaviour to that observed in experiments 1 to 3. A plateau was obtained between irradiation 1 and 2 after 140 days of experiment, corresponding to a production rate of $1.5 \times 10^{-6}$ mol/min. For the following irradiation sequences, no plateau was obtained. Because of the availability of irradiation facility, it was impossible to continue the experiment for longer times than 190 days.

At the end of each experiment, the cells were dismantled. Solid and solutions were separated and analysed (Table 9). For all the experiments, the solutions were clear and after few minutes of contact with atmosphere, a reddish colour occurred and red precipitates of ferric hydroxides appeared. It is obvious that, in spite of the Eh values measured in glove-box or –box, the conditions in the cell were reducing. For the 2 first experiments pH at the end was alkaline (~11), while for experiments 3 and 4 the pH was closed to 9. Solid from experiment 1 was analysed by Raman spectrometry but no transformation (corrosion layer) was evidenced, probably due to quantities below the detection limits.

Table 9: Analysis of solutions at the end of experiment

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Solution</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>pH = 11</td>
<td>Dismantling in glove box measurement in glove bag</td>
</tr>
<tr>
<td></td>
<td>$E_H \sim 80$ mV</td>
<td>Reddish colour after few minutes of contact with atmosphere</td>
</tr>
<tr>
<td></td>
<td>[H2O2] $\sim 0.5$ mg/L</td>
<td>Measured with specific indicators (Merck)</td>
</tr>
<tr>
<td>2</td>
<td>pH = 10.98</td>
<td>Dismantling and measurements in glove bag</td>
</tr>
<tr>
<td></td>
<td>$E_H \sim 13$ mV</td>
<td>Reddish colour after few minutes of contact with atmosphere</td>
</tr>
<tr>
<td></td>
<td>Conductivity = 1.19 g/l</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>pH = 8.8</td>
<td>Dismantling and measurements in glove box</td>
</tr>
<tr>
<td></td>
<td>$E_H &lt; 0$ mV</td>
<td>Reddish colour after few minutes of contact with atmosphere</td>
</tr>
<tr>
<td></td>
<td>[Fe] = $2.7 \times 10^{-5}$ M ($62%$ Fe $^{3+}$, $38%$ Fe $^{2+}$)</td>
<td>Ferrozine method (Viollier et al., 2000)</td>
</tr>
<tr>
<td>4</td>
<td>pH = 8.8</td>
<td>Dismantling and measurements in glove box</td>
</tr>
<tr>
<td></td>
<td>$E_H &lt; 0$ mV</td>
<td>Reddish colour after few minutes of contact with atmosphere</td>
</tr>
<tr>
<td></td>
<td>[Fe] = [Fe $^{2+}$] = $8.3 \times 10^{-6}$ M</td>
<td>Ferrozine method (Viollier et al., 2000)</td>
</tr>
</tbody>
</table>
3.5 DISCUSSION

3.5.1 Step 1 - Corrosion without irradiation

In de-aerated water, anoxic steel corrosion takes place according to:

\[ \text{Fe} + 2 \text{H}_2\text{O} \rightarrow \text{H}_2\text{g} + \text{Fe}^{2+} + 2 \text{OH}^- \quad [1] \]

In the absence of buffering agents, saturation with respect to Fe(OH)\text{}_2 is quickly reached (solubility product \(K_s = 10^{-14.7}\)). Fe(OH)\text{}_2 is unstable under anaerobic conditions and converts to magnetite (Shikorr reaction) at temperature above 80°C (Reardon, 2005):

\[ 3 \text{Fe(OH)}_2 \text{s} \rightarrow \text{Fe}_3\text{O}_4\text{s} + \text{H}_2\text{g} + 2\text{H}_2\text{O} \quad (2) \]

Fe(OH)\text{}_2 converts very slowly at ambient temperatures. However, the conversion can be catalysed by the presence of Fe(0) (Odziemkowski et al., 1998). At ambient temperatures, 10-20 % of ferrous hydroxide are converted in magnetite (Cornell and Schwertmann, 1996). In our experiments, the temperature being low (< 30°C), the corrosion layer is probably constituted of a mixture of iron oxide/hydroxide.

Corrosion rates deduced from these experiments are gathered in Table 10, assuming that corrosion layer is constituted of magnetite (\(\text{Fe}_3\text{O}_4\)) or Fe(OH)\text{}_2. This yields to two corrosion rate values which have to be considered as raw estimates as the plateaus obtained are short and/or approximated. It is worth remembering that such calculated corrosion rates correspond to anaerobic corrosion: aerobic corrosion doesn’t produce hydrogen and is not taken into account in this quantification.

Table 10: \(\text{H}_2\) production rate during step 1

<table>
<thead>
<tr>
<th>EXP</th>
<th>Dose rate (Gy/h)</th>
<th>Particle size(µm)</th>
<th>Duration (days)</th>
<th>(\text{H}_2) flowrate (mol/min.g)</th>
<th>(\text{H}_2) flowrate (mol/m².y)</th>
<th>Anaerobic corrosion rate (µm/y)</th>
<th>(\text{O}_2) (solution) (mol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>&lt;210</td>
<td>1</td>
<td>1.32 (10^{-10})</td>
<td>0.019</td>
<td>0.10-0.14</td>
<td>4.0 (10^{-7})</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>&lt;210</td>
<td>8</td>
<td>3.57 (10^{-10})</td>
<td>0.052</td>
<td>0.28-0.37</td>
<td>4.0 (10^{-7})</td>
</tr>
<tr>
<td>3</td>
<td>11</td>
<td>&lt;10</td>
<td>9</td>
<td>1.6 (10^{-8})</td>
<td>0.041</td>
<td>0.22-0.29</td>
<td>4.3 (10^{-7})</td>
</tr>
<tr>
<td>4</td>
<td>49</td>
<td>&lt;10</td>
<td>90</td>
<td>1.78 (10^{-7})</td>
<td>0.46</td>
<td>2.45-3.28</td>
<td>2.5 (10^{-8})</td>
</tr>
</tbody>
</table>

\(M \text{ Fe} = 10 \text{ g}; V \text{ H}_2\text{O} = 100 \text{ ml}\)

Globally, corrosion rates deduced from experiments 1 to 3 are of the same order of magnitude while experiment 4 shows corrosion rates one order of magnitude higher. For experiments 1-3, corrosion rates, estimated between 2 and 5 µm/y, are globally consistent with values reported in literature (see Stammose and Vokal, 2012a). Reardon (2005) measured the same range of \(\text{H}_2\) production rate (2-6 \(10^{-10}\) mol/min.g) on granular iron (particle size between 200 and 800 µm).

The initial corrosion step without irradiation for experiments 1 to 3 was shorter (between 1 and 9 days) than that of experiment 4 (90 days). Thus, one could have expected that the steady-state was more established in experiment 4, leading to a lower corrosion rate, which is not what was observed. An explanation could be in the redox conditions in the four experiments. The gaseous oxygen content was monitored in the cell above the tested solid/solution systems during all the experiments (see Fig. 38). It shows that for all experiments, the oxygen content decreased rapidly (flushing of the air entrapped during the connection to the experimental device) and then was globally maintained at the same value (steady-state with the solution). The concentration of dissolved oxygen was...
calculated (Henry’s law) for each experiment (see Table 10). For the first experiments (1-3), \([O_2]_{aq}\) was in the same range, close to \(4 \times 10^{-7}\) mol/L, while in experiment 4, the preparation of the cell being conducted in a glove box and the setup connections being further improved, \([O_2]_{aq}\) was lower (~2 \(10^{-8}\) mol/L). This difference in redox conditions all along the experiments could have changed the type of the corrosion layer which formed, leading to a higher passivation in experiments 1-3.

![Fig. 38: Oxygen concentration in the gaseous phase for the four experiments](image)

Other factors (iron particle size, oxide films and hydrogen pressure) are considered below, though they do not directly contribute to explain the differences observed in corrosion rates. Reardon (2005) studied anaerobic corrosion of different granulated iron during 2500 h and observed two styles of corrosion behaviour. One is characterized by a low initial corrosion rate followed by a sharp or gradual increase. The other style shows initial high hydrogen production followed by a decrease, and then a slow progressive increase. For Reardon (2005), coarse grain size and thick oxide coatings can contribute to a delay in hydrogen production whereas thin coatings and fine particle size should induce an early \(H_2\) production.

It is also possible that the composition of iron influences hydrogen production rate. In our experiments, iron was used “as received” and it is possible that some impurities due to its preparation remained at the surface of the grains and modified the solution composition when water was added. But considering experiments 1-3, in which two particle size (<10 and <210 µm) were used, the same corrosion rates have been obtained and it seems that this hypothesis cannot explain the differences in the corrosion rates.

Reardon (2005) also reported that a part of hydrogen produced by corrosion enter the iron lattice, through oxide films or at the interface metal/water inducing an under estimation of its production rate. In our experiments, the pressure inside the cell was close to atmospheric pressure (helium sweeping) and hydrogen trapped in the metal lattice is expected to be very tiny, the amount of hydrogen entering the solid being proportional to partial pressure of hydrogen. For the first step of experiment 4, in which hydrogen accumulated in the cell during 3 months, it is possible that a part of produced hydrogen was trapped in the solid. When the cell was connected to the experimental device, the pressure was reduced and hydrogen desorbed from iron particles inducing variations in hydrogen measurements as observed during the first days following the connection to GC.
3.5.2 Step 2 - Irradiation step: water radiolysis

Our experiments were conducted in “open conditions”, i.e. gas produced was continuously removed from the solution. Therefore, recombination reactions were limited and Allen chain was disturbed inducing hydrogen production by water radiolysis.

As observed in Fig. 34 and Fig. 35 related to experiments 1 and 2, when irradiation began, water radiolysis occurred and the production of hydrogen increased sharply until to reach a plateau. Hydrogen production at the very beginning of the irradiation step, deduced by subtracting the contribution of corrosion (corresponding to step 1) to the values obtained on the plateau, was compared to values obtained by radiolysis of pure water (The comparison between hydrogen production rates calculated according to water radiolysis experiments and those measured in experiments 1 to 3 is presented in Table 11. The production rate calculated for a dose rate of 11 Gy/h is low compared to the production by corrosion (1.6 10-7 mol/min for 10 g) and cannot be detected. The values deduced from experiments at 50 and 100 Gy/h (experiment 1 and 2) are slightly higher than those calculated. Moreover, H2 produced by radiolysis being proportional to the dose rate, a factor 2 between the two experiments is expected instead of 1.3.

Table 11), so as to verify that this hydrogen production is strictly due to radiolysis of the solution.

In order to determine H2 production by pure water radiolysis, we have carried out a set of irradiation of 100 ml de-aerated water (Millipore quality) at different dose rates, with the same device than for experiments 1-4, i.e. H2 produced in solution was transferred to the gaseous phase through helium sweeping. The variation of H2 production as a function of dose rate is presented in Fig. 39.

![Graph showing hydrogen production vs dose rate](image)

**Fig. 39: Hydrogen production by water radiolysis in mol/min versus dose rate (Gy/h)**

Hydrogen production is proportional to the dose rate \( \text{H}_2 \text{ (mol/min) } = 10^{-10} \times \text{Dose Rate (Gy/h)} \). At the beginning of the experiment, without irradiation, a tiny hydrogen production was observed which is interpreted as due to a residual presence of iron particles. At the end of irradiations, the same hydrogen production was measured. This pollution seems sufficiently low to be without effect on hydrogen production by water radiolysis.
The comparison between hydrogen production rates calculated according to water radiolysis experiments and those measured in experiments 1 to 3 is presented in Table 11. The production rate calculated for a dose rate of 11 Gy/h is low compared to the production by corrosion (1.6 $10^{-7}$ mol/min for 10 g) and cannot be detected. The values deduced from experiments at 50 and 100 Gy/h (experiment 1 and 2) are slightly higher than those calculated. Moreover, H$_2$ produced by radiolysis being proportional to the dose rate, a factor 2 between the two experiments is expected instead of 1.3.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Dose rate (Gy/h)</th>
<th>Measured H$_2$ (mol/min)</th>
<th>Calculated H$_2$ (mol/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>11</td>
<td>-ND-</td>
<td>1.1 $10^{-9}$</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>1.03 $10^{-8}$</td>
<td>5 $10^{-9}$</td>
</tr>
<tr>
<td>1</td>
<td>100</td>
<td>1.36 $10^{-8}$</td>
<td>1 $10^{-8}$</td>
</tr>
</tbody>
</table>

Joseph et al. (2008) observed an increase of hydrogen production (x10) when dissolved oxygen is present in solution ($2.5 \times 10^{-4}$ mol/L). At the beginning of irradiation, the oxygen content in experiments 1 and 2 was quite similar (≈4 $10^{-7}$ mol/L) and the possible influence of oxygen on hydrogen production by water radiolysis could have been the same. Joseph et al. (2008) also observed an increase in both H$_2$ and H$_2$O$_2$ production for pH higher than 10. In order to test a possible enhancement of hydrogen production in basic conditions (pH=11 at the end of experiments 1 and 2), we irradiated 100 ml of NaOH $10^{-2}$ M. H$_2$ production was similar to those obtained for pure water and the same relation between H$_2$ (mol/min) and dose rate (Gy/h) was obtained.

Another explanation could be the enhancement of the decomposition of water under irradiation in presence of solids like oxides. Different authors have observed that γ-radiolysis of water in heterogeneous systems constituted of oxides and water induces an enhancement of H$_2$ production compared to pure water (Laverne and Tonnies, 2003, LaVerne and Tandon, 2002, Yamada et al., 2011). Both nature of oxides and specific area seem important parameters but until now mechanisms are not elucidated (Jonsson et al., 2007). Complementary experiments would be necessary to precise the role of iron oxides in water radiolysis processes (irradiation of water in presence of different iron oxide like magnetite, hematite...).

The presence of Fe(II) in solution induces also an increase of hydrogen production (Bouniol, 2013). Actually, H$_2$ production rate by water radiolysis is constant at a constant dose rate but the water decomposition rate is very sensitive to aqueous environments including corrosion products (Yakabuskie et al., 2010). Radicals OH$^-$ produced by water radiolysis can react with Fe$^{2+}$ according to the following reaction (Jonsson, 2010):

$$Fe^{2+} + OH^- \rightarrow Fe^{3+} + OH^- \quad (R5) \quad k = 3.2 \times 10^8 \text{ L.mol}^{-1}.\text{s}^{-1}.$$

Considering the kinetic of this reaction (R5) which is very fast, the decomposition of H$_2$ through reaction R1 (see Table 6) cannot occur, Allen chain is disturbed and a large part of radiolysis products such as H$_2$ and H$_2$O$_2$ are preserved from recombination reactions.

With the objective to test this last hypothesis regarding an influence of Fe(II) in solution on our experiments, we performed irradiation experiments at different dose rate of 100 ml of solution containing FeSO$_4$ at a concentration of 2.3 $10^{-3}$M with the same experimental device. Like for
irradiation experiments of H$_2$O, hydrogen production was observed in absence of irradiation probably due to residual iron pollution.

A linear relationship was obtained between H$_2$ (mol/min) and dose rate (Fig. 40). These data show that as soon as ferrous ion is present in solution, hydrogen production by water radiolysis is higher (x5) than in the case of pure water whatever the tested dose rate. Considering the duration of corrosion step of experiment 1 and 2, respectively 1 and 8 days, the content of ferrous ion in the solution was probably higher in experiment 2, which is consistent with the hydrogen production rate higher than expected (1 $10^{-8}$ mol/min instead of 5 $10^{-9}$ mol/min expected). Therefore the increase of hydrogen production under irradiation is not directly proportional to dose rate as far as there are differences in ferrous ion concentration in solution.

![Fig. 40: Hydrogen production by FeSO$_4$ solution radiolysis in mol/min versus dose rate (Gy/h)](image)

For experiments 3 and 4, no increase of hydrogen production was observed when irradiation began. In both cases, the production of hydrogen produced by corrosion was much higher (respectively 1.6 $10^{-7}$ and 1.8 $10^{-6}$ mol/min) than expected by pure water radiolysis (respectively $10^{-9}$ and 5 $10^{-9}$ mol/min), so that the H$_2$ production by water radiolysis cannot be distinguished.

We can note that for experiments 1 and 2, the decrease of H$_2$ production observed when irradiation was stopped, was of the same amplitude than that of the increase observed at the beginning of irradiation. This validates the fact that the observed variations are directly related to water radiolysis. Nevertheless, the amount of soluble iron being increasing with time, we cannot exclude a slightly higher hydrogen production by water radiolysis at the end of the irradiation step. This could lead to a slight overestimation of the corrosion rate at the end of the corresponding irradiation phase, as this corrosion rate is calculated by subtracting the contribution of water radiolysis observed at the beginning of the irradiation phase to the measured value of hydrogen production rate at the end of this phase.
3.5.3 Step 2 and Step 3: Corrosion under and after irradiation

Whatever the total duration of the experiment (between 30 and 190 days), no plateau was obtained neither during irradiation phase, neither when irradiation was stopped.

The variations in H$_2$ production rate (expressed in mol/y.m$^2$) versus time are plotted in Fig. 41. The contribution of water radiolysis in experiments 1 and 2 is withdrawn in order to compare the corrosion processes of iron under irradiation. For experiments 1 and 2, pseudo plateaus were obtained, but were always followed by a continuous increase of hydrogen production continuing when irradiation was stopped. For experiment 3 no significant variation in hydrogen production was observed during irradiation steps.

![Fig. 41: Variations of hydrogen production versus time for experiments 1-3](image)

We have compared hydrogen production rate between 22 and 30 days (Fig. 42), this period corresponding to steady H$_2$ variations for the three experiments.
Fig. 42: H$_2$ production between 22 and 30 days for experiments 1, 2, 3.

The slopes deduced from linear regressions on the 3 curves are gathered in Table 12. The slope increases with dose rate (Fig. 43) and total dose (see Table 12) but this would worth being confirmed by other experiments carried out with other dose rates.

Table 12: Increase factor of hydrogen production rate for the 3 experiments

<table>
<thead>
<tr>
<th>Dose rate (Gy/h)</th>
<th>Total dose (Gy) received after 22 days</th>
<th>Slope (mol/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1.6 $10^3$</td>
<td>5.75 $10^{-6}$</td>
</tr>
<tr>
<td>50</td>
<td>14.6 $10^3$</td>
<td>2.44 $10^{-5}$</td>
</tr>
<tr>
<td>100</td>
<td>50.4 $10^3$</td>
<td>2.56 $10^{-5}$</td>
</tr>
</tbody>
</table>

Fig. 43: Evolution of H$_2$ production rate versus dose rate

As reported previously (§ 0 in this report) different mechanisms may induce this increase in H$_2$ production rate.

For a reactive material such as iron, the redox conditions are established by the interactions between reactive radiolysis products (H$_2$O$_2$, OH$^*$), the steel surface and the corrosion products produced by these reactions. First, if radicals can induce transitory enhancement of corrosion, considering their residence times ($10^{-7}$ s), their influence on iron corrosion is expected to be limited to the irradiation period. Therefore, the observed increase in hydrogen production rate is not likely linked to direct oxidative role of radicals. Second, OH$^*$ radicals are also generated by a reaction between H$_2$O$_2$ and ferrous ions according to the Fenton reaction. The kinetics of this reaction is slow, and thus could take place after the end of irradiation. However, the amount of radicals formed by this reaction is probably very low and their contribution to iron corrosion would be limited.

Third, hydrogen peroxide appears as an active species towards carbon steel. Daub et al. (2010) observed that the addition of H$_2$O$_2$ in multiple steps (progressive addition) to carbon steel matched the behaviour of carbon steel under irradiation. In the conditions of their experiment (dose rate = 6.8
kGy/h, irradiation during 6 h, pH=10.6), they concluded that H₂O₂ is the key radiolysis product, radical species being of minor importance. Daub et al. (2010) also measured an increase of the corrosion potential (Ecorr) during irradiation, from ~ -0.65 V (vs SCE) potential value close to 0 V regardless the pre-existing oxides present on carbon steel surface. The lower potential value corresponds to the oxidation of Fe (0) to Fe II oxide/hydroxide and/or magnetite (Fe₃O₄), while the higher potential corresponds to a mixture of magnetite/maghemite (γ-Fe₂O₃) (Daub et al. 2011). These observations were confirmed by solid observations (Raman Spectroscopy). This transformation may be accompanied by the creation of some defects in the corrosion layer which reduce the protective role of this layer towards corrosion.

The amount of H₂O₂ produced by water radiolysis depending on γ irradiation dose rate, Daub et al. (2010) also investigated the influence of H₂O₂ concentration (10⁻⁶ -10⁻² mol/L) on the reactions between hydrogen peroxide and iron carbon steel. For low H₂O₂ (< 10⁻³ mol/L) concentration, H₂O₂ acts directly as an oxidant towards steel and the oxide layer, while for high H₂O₂ concentration (> 10⁻³ mol/L), hydrogen peroxide decomposes on carbon steel and its surface film (catalysts) according to the reaction:

\[ 2 \text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2 \text{H}_2\text{O} \]

The kinetics of H₂O₂ decomposition depends mainly on experimental conditions such as pH, concentration of hydrogen peroxide and on the catalyst (here the corrosion layer) structure (Lin and Gurol, 1998, Fu, 2008). The production of oxygen by hydrogen peroxide decomposition induces a modification of the steady state concentration of radiolysis products and an increase of H₂ production as those observed in experiments 1 and 2 (Joseph et al., 2008). However, this H₂ production stops as soon as irradiation is stopped and cannot explain the continuous increase observed in our experiments when irradiation was stopped. Besides, the decomposition occurs at the surface of the corrosion layer and oxygen may induce some localized oxidation and therefore a loss of protective properties of the corrosion layer. The reconstruction of this corrosion layer might take some time, probably longer than the radiolytic processes in solution. This hypothesis would worth being further investigated.

Globally, both above mentioned mechanisms, i.e. direct and indirect interactions with the steel and its oxide layer may have occurred in the experiments 1-3.

In experiment 4, the behaviour of the system is different from that observed in experiments 1-3: hydrogen production rate decreased when irradiation was applied and increased when irradiation was stopped. Like in all the experiments, no plateau was obtained. The main difference of this experiment comparing to the others was the oxygen content in the solution (10 times lower) and the 90 days of corrosion in the closed cell before to connect it to the flushing experimental device. Hydrogen production by iron corrosion was higher (0.46 mol/m².y) than for the previous experiments (0.02-0.05 mol/m².y) and hydrogen produced by water radiolysis was too low to be detected (10⁻⁸ mol/min for 100 ml of water).

For this oxygen concentration, the corrosion layer formed at the surface of the steel may be different, in composition and structure, from those obtained with higher oxygen contents. This could explain the difference in behaviour towards irradiation compared to experiments 1-3. Besides, the higher H₂ production in this experiment 4 compared to experiment 1-3 may modify the radiolysis processes and therefore modify the steady state concentrations of radiolytical species; this could lead to difference in corrosion rate under irradiation but does not explain the behaviour of the system in the steps without irradiation. At last and surprisingly, the pH of experiment 1 and 2 was alkaline (~11) while that of experiments 3 and 4 was close to 8. Until now, no satisfactory explanation has been found to these high pH values.
Globally, further investigations are needed to understand the processes behind the observations made from these four experiments. These investigations have to be conducted for longer times (> 3 months) in well controlled conditions (particularly oxygen content) with carbon steel pieces (instead of granular iron) in order to control the initial state of the tested samples (same corrosion state). The characterisation at the end of experiments of solids (by spectroscopy techniques like Raman, SEM) and solutions (redox potential, soluble iron speciation, hydrogen peroxide concentration) should allow further assessing the processes involved in corrosion under irradiation. At last, similar experiments should be conducted with solutions representative for conditions expected in an underground disposal in a clay formation, i.e. in clay pore water containing ionic species sensitive to irradiation like carbonate and chloride.

3.6 CONCLUSION

The studies performed in FORGE Work Package 2 aimed at further assessing the effects of parameters representative of repository conditions (T, Eh, reactive surface, solid and/or liquid phases in contact with steel, irradiation…) on hydrogen production rates and consequently on corrosion rates of carbon steel. The experiments carried out by UJV consisted in measuring continuously the volume of hydrogen generated from iron powder or carbon steel samples of various reactive surfaces in synthetic bentonite pore water, within a closed system at various temperatures (40 to 80°C) and anaerobic conditions. In addition, a series of experiments was performed in presence of compact bentonite. The effect of irradiation was assessed by IRSN using iron powder in de-aerated pure water, in an “open” (flushed) system with continuous monitoring of hydrogen production by gas chromatography, for three dose rates (11, 50 and 100 Gy/h).

A rather large range of hydrogen production rates was measured, with initial rates up to 10 molH₂.m⁻².yr⁻¹ and rates after formation of a corrosion layer from 0.02 to 6 molH₂.yr⁻¹.m⁻² (corresponding to corrosion rates in the range 0.1 to 30 µm/yr approximately) depending on conditions of corrosion. Though most of the experiments were carried out on short durations (30 days), a 1-year experiment based on hydrogen continuous measurements as well as on weight loss measurements after dismantling, leads to values within this range, with a steady state value of 1 mol.m⁻².yr⁻¹ corresponding to about 5 µm/yr.

Globally, WP2 experiments show that reactive surface area acts on hydrogen generation rates through its effect on the evolution of redox conditions as a result of corrosion, which conditions impact the stability of the corrosion layer. An important parameter is thus the ratio of surface of metals to the volume of water, as it primarily affects the oxidation potential of water in contact with metals: while the (slight) presence of oxygen impacts hydrogen generation rates at the beginning of corrosion until a sufficiently protecting layer is formed, strongly reducing environment can also favour hydrogen generation, possibly as the stable corrosion product layer cannot be reproduced after dissolution.

Besides, the oxygen content in the surface layers of corroded samples was found to be higher than the stoichiometric ratio of Fe/O in magnetite or maghemite, suggesting that the composition of passive corrosion products layers is not only formed by an inner layer of magnetite and outer layer of maghemite as proposed in previous papers.

A strong enhancement effect of temperature (40 to 70°C) on hydrogen generation rate was shown at the very beginning of the corrosion process: the higher the temperature is, the higher the initial hydrogen generation rate. Then, the temperature effect depends on the nature and stability of the corrosion layer. Globally, WP2 experiments show that hydrogen generation rate is not proportionally related to temperature (in the tested range), except at the very beginning of the corrosion process.
Though measured data tends to indicate that effect of temperature on hydrogen generation rate (corrosion rate) is not a significant issue for post-closure assessment, there is not large statistical set of data from long-term experiments to prove it.

Bentonite in the solid form emplaced in a permeable bag added to the solution leads to a slight increase in the hydrogen generation rate form iron powder. On the contrary, the average corrosion rate of a carbon steel cylinder in contact with compacted bentonite after 30-days experiments was one order of magnitude higher compared to those measured in solution without bentonite. Such an increase due to a direct contact between carbon steel and compacted clay, consistent with previous studies (King, 2008), may be due to sorption of iron species onto bentonite which thus do not contribute to the formation of an adherent corrosion layer. As a consequence, one can expect that this effect of compacted bentonite would decrease with time and consider that the measured corrosion rate is not incompatible with other prior studies, which recommend considering a rate of a few µm/a for far longer periods of corrosion.

Regarding hydrogen production rate under irradiation, opposite effects of irradiation were observed, either an increase (50 and 100 Gy/h) with a significantly enhanced production of hydrogen (x 10) or a decrease (11 Gy/h) in hydrogen production for the higher measured production. Furthermore, the increase in hydrogen production was sustained when irradiation ceased. Different mechanisms were investigated to explain these results. Oxygen content in the solution appears as a key parameter by controlling the type of corrosion layer and in turn hydrogen production rate due to corrosion, though it cannot explain solely the continuous increase in hydrogen production. Thus, molecular radiolytical species like hydrogen peroxide were probably involved in direct or indirect oxidation reactions towards iron or corrosion layer and initiate corrosion mechanisms which last after the irradiation period. However, despite the various verifications made (hydrogen production by water radiolysis, effect of the presence of aqueous iron ...), uncertainties remain either on the experimental side due to the strong constraint of both irradiation conditions and precise continuous measurement of hydrogen or on the theoretical side, so that no attempt to explain the observations was fully satisfactory.

More generally, the work carried out in FORGE Work Package 2 suggests that hydrogen generation rates cannot be accurately predicted if exact corrosion conditions and their evolution in space and time are not known. However, ranges of hydrogen generation rates for different periods of time can be derived validly from the existing state-of-knowledge, the thermo-hydraulical transient period being associated to larger uncertainties. This may be acceptable for gas migration assessment purposes, depending on the sensitivity of the predominant gas migration processes to the gas source term (this sensitivity may vary from one disposal concept to another), on the importance of the transient period with respect to the issue of concern (hydraulic and/or mechanical perturbations...), as well as on the uncertainty management approach in the safety case (sensitivity analyses, normal and altered/degraded scenarios). Further investigation and understanding on the gas generation issue would be necessary if the uncertainties remain too large with respect to the assessment of gas migration and in turn of its potential hydro-mechanical consequences. At last, regarding the effect of irradiation, no conclusion could be reached with regard to carbon steel corrosion rates. Beyond the need for additional research in this field, this raises the question of whether irradiating conditions at the carbon steel container extrados should be excluded by design, for those containers with tightness required for hundreds years.
4 References


Stammose, D., Vokal, A., 2013. FORGE WP2 - Progress report. FORGE Report D2.4. 31pp


