State of the Art - Experiment Specifications and Validation of Experimental Devices

FORGE Report D2.1– VER.0

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Compiled	Virginie Wasselin–Trupin	IRSN		19th April 2010
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Euratom 7th Framework Programme Project: FORGE

EURATOM

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:

Virginie Wasselin–Trupin

Organisation IRSN

Tel: (33)1 58 35 86 85 Fax (33)1 58 35 79 76

email: virginie.wasselin-trupin@irsn.fr

web address: www.irsn.org

Address IRS[N] DSU/SSIAD/BECID

BP 17

92262 Fontenay aux Roses

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Introduction

It is well known that the largest source of gas in a repository will come from anaerobic corrosion of iron canisters. Despite a huge number of publications devoted to the study of iron and carbon steel corrosion mechanisms under various conditions, there are a lot of uncertainties concerning hydrogen evolution rate in a repository from this source. Especially, there are some discrepancies in respect of the effect of content of oxygen, carbon oxide, or chemistry of groundwater. There is very little information on the effect of radiation on mechanism of iron corrosion in anaerobic conditions and hydrogen evolution rate.

1.1 CORROSION

This part of the state of the art report is devoted to the review of known information on iron corrosion in respect to hydrogen evolution rate. It will serve primarily for interpretation of experimental results, which are focused on measuring of hydrogen evolution rate under various conditions from iron and carbon steel corrosion.

1.1.1 Corrosion mechanisms of iron and carbon steels

The character of corrosion mechanisms of iron and carbon steels depends primarily on the content of oxygen in a groundwater contacting canisters. From this point, DGR evolution phases can be divided as follows:

- **Aerobic phase** - during the operation phase of a repository and some time after its closure, the overall aerobic corrosion reactions will occur in the unlimited presence of oxygen trapped in the buffer and backfill materials with sufficient flux of oxygen from unsaturated environment (~8 ppm of O_2). No hydrogen is generated in the phase.
- **Limited flux of oxygen –** phase (0.03 – 8 ppm of O_2) the buffer is assumed to be saturated with groundwater, so that the mass transport of oxygen to and from the canister surface is by diffusion through water-filled pores. Hydrogen can be generated depending on the contact of oxygen in groundwater.
- **Anaerobic phase** - after consumption of oxygen (< 0.03 ppm of O_2). Corrosion is connected with hydrogen generation.

The time scales of the individual phases will depend on the host rock environment and the design of the repository.

1.1.1.1 AEROBIC PHASE

Corrosion of canisters starts immediately after their manufacture in the atmosphere of storage facilities. The character of corrosion mechanism will depend primarily on the humidity of the air in storage facilities. After achieving so-called “critical relative humidity” (CRH), a continuous film can be formed on metal and corrosion goes in aqueous phase. Achieving of CRH depends on the type of metal, and other conditions. Dry oxidation phase leads to the steady build up of an oxide layers. In general, the thicker is the oxide layer, the slower is the subsequent oxidation rate. The detailed character of oxide layer depends, however, on the content of air contaminants: mainly the content of sulphur and nitrogen oxides.

After achieving critical relative humidity, corrosion of carbon steels goes in aqueous phase and is 10 to 100 times higher than corrosion in dry phase. In bentonite environment, the critical relative humidity will be achieved very quickly.

The corrosion of iron in pure water under aerobic conditions can be expressed by the following equation:

$$4\ Fe + 2\ H_2O + 3\ O_2 \rightarrow 4\ FeO(OH) \rightarrow 2Fe_2O_3 + 2H_2O \qquad (1)$$

It is supposed that no hydrogen is formed under this phase. From thermodynamic point of view the driving force (Gibbs energy = -1374 kJ/mol) of this reaction is very favourable and the reaction is thus practically irreversible. The solubility of formed iron-oxyhydroxides and iron oxides is very low and if no constant removing of solid products would proceed, the general corrosion rate would very quickly slow down due to corrosion products constraints.

Under some conditions, primarily a high redox potential difference, very adherent and covering solids may be formed on the surface of iron, especially in the alkaline environment. These solid products will passivate the metal and the corrosion will practically decrease to negligible values. The presence of carbonates can contribute significantly to the formation of passive layers on the surface of iron. Problem is that a passive film formed can be breached resulting in localized forms of degradation, such as pitting, crevice corrosion, stress-corrosion cracking (SCC), or hydrogen embrittlement (HE). The rate of localized corrosion is of rates many orders of magnitude higher than the rate of general corrosion. The tendency of iron to passivation depends primarily on the iron additives. Passivation layers are formed very quickly if the content of Cr is higher than 12 %. To the formation of passivation layers contributes also elements like Mo or Ni, but the anions like Cl^- or SO_4^{2-} disturb the passive layers.

1.1.1.2 AQUEOUS CORROSION WITH LIMITED FLUX OF OXYGEN

After emplacement of the canisters in DGR, and after sealing all the paths to atmosphere, the bentonite will gradually saturate with water and the concentration of trapped oxygen will be reduced by corrosion and microbial reactions. It is supposed (Marsh et al., 1987) that three following sources of oxygen will be in the repository after its closure:

- The air trapped in the pore space of buffer and backfill material
- Dissolved oxygen in the groundwater permeating the repository
- Oxygen formed by radiation

It was reported (Marsh et al., 1987) that this period is indefinite if the diffusion coefficient of oxygen in bentonite is 1.2 x 10^{-10} m^2 s^{-1} and about 130 years if the diffusion coefficient is 1.2 x 10^{-11} m^2 s^{-1}. The authors, however, assume - very conservatively - that the concentration of oxygen at the floor of repository tunnels remains very high (8 ppm) and constant. This condition is however, as was shown in recent REX project (Puigdomenech et al., 2000, 2001), unrealistic high mainly due to microbial consumption of oxygen during its way to deep groundwater.

In the bentonite environment, diffusion coefficient of oxygen is decreasing with bentonite density according to Manaka, 2000 (Fig. 1) and therefore the effect of oxygen reactions will quickly decrease.

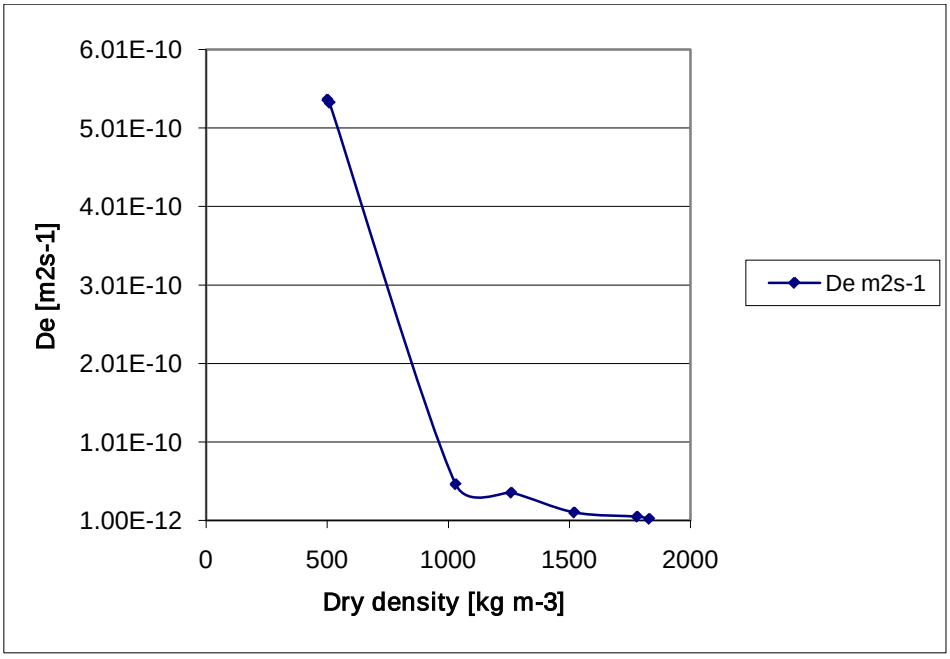

Figure 1: The change of diffusion coefficient for oxygen on density of bentonite

It is supposed that only under the presence of oxygen, a sufficiently high potential might be generated leading to the passivation of carbon steel surface and possible localized corrosion. The current approaches (Dunn et al., 2000, Druyts et al., 2001) for evaluating the tendency of iron and iron alloys (stainless steels) to localized corrosion are based on determining characteristic potentials of polarisation curves. Values of critical potential for pit nucleation (E_{np}) and critical potential for repassivation (E_{pp}) (protection potential) are compared with the values of corrosion (open circuit) potential (E_{corr}). If E_{corr} exceeds $E_{np,}$ pits will initiate and grow. If E_{corr} is between E_{np} and E_{pp} existing pits will grow but no new ones will be formed and mechanical damages to a passive layer will give rise to localised corrosion and occurring crevice corrosion will also continue. For E_{corr} below E_{pp} all pits will repassivate. It seems that in the environment without oxygen, corrosion potential E_{corr} is very low and therefore it not very probable that some type of localized corrosion could be important, but it can be supposed that a very low concentration of oxygen the passive film cannot be reproduced sufficiently and therefore the corrosion rate becomes higher.

It is supposed that during this phase hydrogen can be generated by reactions described below.

1.1.1.3 AQUEOUS ANAEROBIC CORROSION

After some time depending on a number of factors, which affects decay of oxygen in surrounding environment, iron will corrode without any oxygen through the following reaction.

$$Fe(s) + 2H_2O \leftrightarrow Fe(OH)_2(s) + H_2(aq) \quad (2)$$

Ferrous hydroxide is not stable and can easily decompose by so-called Shikorr reaction to magnetite leading again to the formation of hydrogen.

$$3Fe(OH)_2(s) \leftrightarrow Fe_3O_4(s) + 4H_2(aq) + 2H_2O \quad (3)$$

Above 85 ^{o}C iron hydroxide is decomposed through the following reaction without hydrogen evolution

$$4Fe(OH)_2(s) \rightarrow Fe_3O_4(s) + Fe(cr) + 4H_2O \quad (4)$$

The Schikkor reaction is very slow under temperatures about 60 °C.

Reaction (3) is very often used for recalculation of hydrogen evolution rate from measuring corrosion rate form example by weight loss measurement. The following equation was used for recalculation of corrosion rate on hydrogen evolution rate

$$v_{H_2} = S \times R \times \rho \times m \times \frac{1}{M_{Fe}/1000}$$

vhere v_{H2} is hydrogen generation rate mol/year, S is reactive surface area (m^2), R is corrosion rate m/year, ρ is density of iron, m is stoichiometric factor (4/3) for the generation of magnetite (equation (3)) and M_{Fe} is molecular weight of iron (55.85 g/mol).

(In some older publications the results of hydrogen evolution rate were given in ml m^{-2} d^{-1}. The rate in units of mol m^{-2} yr^{-1} can be obtained by dividing the value by number 61.41.)

1.1.2 Carbon steel corrosion and hydrogen evolution rates under repository conditions

A number of experiments have been devoted to the measurements of carbon steel corrosion and hydrogen evolution rates, (Jelinek, Neufeld, 1982, Simpson, 1984, Simpson et al., 1985, Anantamula et al. 1987, Marsh, Taylor, 1988, Schenk, 1988, Grauer et al., 1991, Hara et al., 1992, Honda et al., 1991, Kozaki et al., 1994, Fujisawa et al.1997, Xia et al., 2005, Smart et al., 2001, 2008), and reviews (Platts et al., 1994, Wiborgh et al., 1986 under simulated repository conditions.

Jelinek and Neufeld (1982) measured the hydrogen evolution from carbon steel in pure water or in 0.1 N $NaHCO_3$ solution using gas chromatography methods in the temperature range between 60 and 100 °C. Various amount of copper was also added to the solution as a potential catalyst of the reactions leading to the hydrogen evolution. The results of their measurements are given in the following Table 1.

Table 1: Hydrogen formation rates at various conditions (Jelinek, Neufeld, 1982)

Solution composition	Hydrogen evolution ($molm^{-2}yr^{-1}$) 60 °C	Hydrogen evolution ($molm^{-2}yr^{-1}$) 80 °C	Hydrogen evolution ($molm^{-2}yr^{-1}$) 90 °C	Hydrogen evolution ¨ ($molm^{-2}yr^{-1}$) 100 °C
Distilled water	0.18	0.2	0.15	0.29
Dist. Water + 0.2 ppm Cu		0.31		
Dist. Water + 1 ppm Cu	0.38	0.20	0.07	
Dist. Water + 1 ppm Cu	0.34	0.33	0.12	
0.1 N $NaHCO_3$	0.14	0.59	0.07	
0.1 N $NaHCO_3$ + 10 ppm Cu	0.07		0.1	
0.05 N $KClO_3$	0.28			

Hydrogen evolution rate was correlated with corrosion rates determined by the weight loss. They found that the average rate of hydrogen evolution at temperatures below 100 °C in distilled water was about 0.16 mol/m^2/yr. The value of 0.29 mol/m^2/yr at 100 °C given in the Table 1 comes from an older paper of Gould and Evans (1947). A much lower corrosion rates were predicted using hydrogen evolution (0.8 μm/yr – 0.15 molm^{-2}yr^{-1}) than through weight loss measurements (1.3 μm/yr - molm^{-2}yr^{-1}). Jelinek and Neufeld (1982) did not find any temperature dependence in the range 60 to 316 °C under the measurement conditions and no catalytic effect of copper.

Simpson and Schenk (Schenk, 1988, Simpson, 1984, Simpson et al., 1985) measured hydrogen evolution in real granitic waters from sites Säckingen and Böttstein and in sodium chloride solutions at temperatures 25, 50 and 80°C and various pH. They used similar chromatographic method of hydrogen quantification as Jelinek and Neufeld (1982). The initial values for hydrogen evolution from real granitic waters achieved very high values about 27.36 mol/m^2/yr, but after a short time these high values decreased to values given in the Table 2.

Table 2: Hydrogen evolution from corrosion of iron in real granitic water (Simpson et al., 1985)

Type of granitic water	25 °C (mol/m^2/yr)	50 °C (mol/m^2/yr)	80 °C (mol/m^2/yr)
Böttstein	0.18	0.98	0.37
Säckingen	0.25	0.51	0.23

The results of hydrogen evolution rate measured by Simpson in dependence of concentration of Cl^- and two temperatures 80 and 50°C are plotted in the following Fig. 2

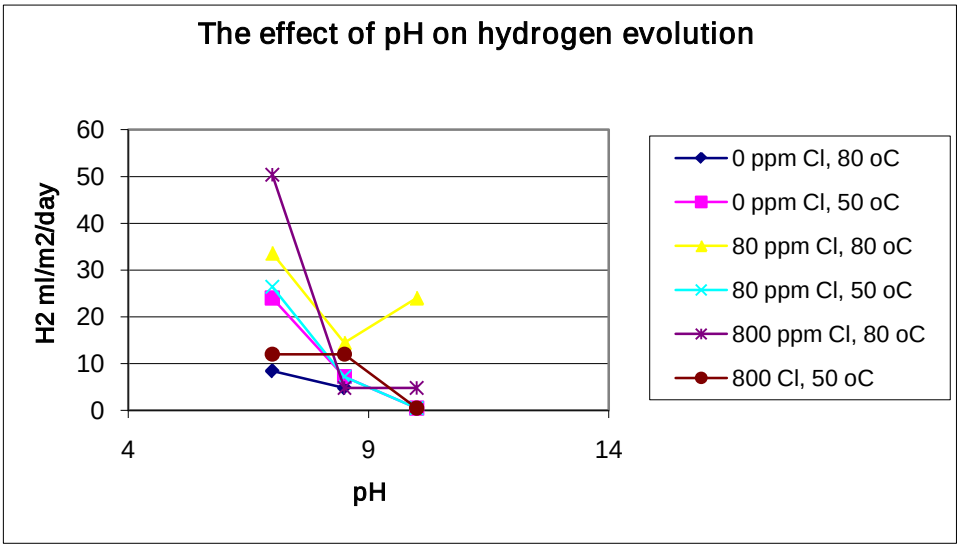

Figure 2: The effect of pH on hydrogen evolution

It follows from this figure that hydrogen evolution depends significantly on pH. The effect of temperature does not seem to be significant. The data suggest that there could be some temperature (about 50 °C) at which the hydrogen evolution is maximal. The effect of chloride ions concentration is negligible within the range studied. From a comparison of the data in the table 1 and 2 can be derived that the hydrogen evolution rate of carbon steels in the granitic water could achieve more than five times larger values than in distilled water.

In the same water as Simpson and Schenk (Schenk, 1988, Simpson, 1984, Simpson et al., 1985) from the Böttstein site, Grauer et al. (1991) measured hydrogen evolution at 25°C using equipment based on the measurements of change of volume. They found contrary to the results of Simpson and Schenk (Schenk, 1988, Simpson, 1984, Simpson et al., 1985) that the initial rate of hydrogen evolution is only 0.07 $molm^{-2}yr^{-}1$ under the same compositions of groundwater. This value further decreased to a steady-state value of about 0.005 $molm^{-2}yr^{-1}$after more than 8000 hours.

At about pH 10, carbon steels evidently passivate and hydrogen evolution is negligible. The similar results on the passivity of carbon steel at higher pH were observed also in the papers of Matsuda et al. (1995) or Fujiwara et al. (2001).

Marsh and Taylor (1988) performed laboratory tests of carbon steel corrosion covered with either crushed granite or bentonite paste to depths of 5, 7.5 or 10 cm in synthetic granitic water. Three types of steel were included in the programme: a forged steel, a cast steel and a low carbon forged steel. Average corrosion rates from experiments, which lasted more than 3 years, were in the range 1.7 to 7.7 μm/yr in bentonite and 19.2 to 26 μm/yr in granite. The corrosion rate was determined from weight loss measurements. The corrosion rate of the cast steel was 3-4 times less than the forged steel in bentonite, although there was little to distinguish their behaviour in granite. Only general attack occurred in bentonite. Bentonite specimens were covered by an adherent ~ 0.1 mm layer of bentonite + corrosion product which spalled when it dried out. Visually there was a definite colour change in the bentonite approximately 4.5 cm inward, suggesting this marked region became contaminated with corrosion products. Without the presence of oxygen Marsh and Taylor (1988) strongly suggest that the corrosion rate of carbon steels will be well below 1 μm/yr (0.2 $molm^{-2}yr^{-1}$) at temperatures below about 50 °C.

Hara et al. (1992) measured hydrogen evolution from carbon steel under various concentration of oxygen. They found that the volume of hydrogen gas generated tends to increase with increasing dissolved oxygen concentration and this tendency was more noticeable after 30 days immersion of specimens than at 14 days immersion. The average hydrogen evolution was about 0.54 $molm^{-2}yr^{-1}$ at the concentration of oxygen of 0.01 ppm, but was more than 21.2 $molm^{-2}yr^{-1}$ at the concentration of 10 ppm of oxygen. They suppose that this is caused by hydrogen evolution in the pits of localized corrosion that occurs in solution with the higher oxygen concentration.

Fujisawa et al. (1997) measured hydrogen evolution from carbon steel wires in mortar water (pH = 12.6), in aqueous solution saturated with calcium hydroxide (pH = 12.8) and in synthetic groundwater with bentonite powder (pH = 8) at three temperature: 15, 30 and 45 °C. The content of oxygen was below 0.06 mg/l. The hydrogen evolution was high at initial period, but was very low after this period. They found a very distinct effect of temperature on hydrogen evolution. The activation energy of corrosion in alkaline water was about 18 kJ/mol. In alkaline (mortar) water, the corrosion rate decreased with time. In contrast, in synthetic groundwater hydrogen gas was generated at a constant rate. The difference in behaviour was explained by the fact that in synthetic groundwater, below pH 9.5, no passive film is formed.

Fujiwara et al. (2001) also observed that for oxygen concentration 100 ppb the evolution of hydrogen from carbon steels increases with an increase of oxygen concentration. They also suppose as Hara et al. (1992) that this is caused by an increase of the localized corrosion area. But under sufficiently reducing conditions, it has been found that generation of hydrogen tends to increase when the oxygen concentration is lower. It was explained as follows: when a passive film is produced on the surface of carbon steel, the generation of hydrogen extremely decreases to the equivalent corrosion rate of 0.01 μm/year or less. However, under a very low concentration of oxygen the passive film cannot be reproduced sufficiently and therefore the corrosion rate becomes higher. They suppose that air passive film, formed by Fe_2O_3, changes to Fe_3O_4 by the dissolution of Fe_2O_3 as a complex ion $HFeO_2$, which in turn produces Fe_3O_4 by reaction with H^+.

Smart et al. (2001) used the similar experimental techniques for measuring of hydrogen evolution in the artificial KBS TR 36 groundwater water at 30 and 50 °C as Grauer et al. (1991). He also observed as Grauer et al. (1991) or Simpson and Schenk (Schenk, 1988, Simpson, 1984, Simpson et al., 1985) very high values about 3.3 $molm^{-2}yr^{-1}$ in the beginning of experiments. To investigate the effect of oxide

formation on metal surfaces, they artificially covered carbon steel wires with magnetite or carbonate layers. They found that both films were able to reduce the initial burst in the hydrogen production rate that was observed on pickled metal surfaces. The thick magnetite film specimens showed very little corrosion during the first 100 hours. At all times the rates of hydrogen evolution were below those measured on unfilmed (i.e. pickled) specimens at comparable times. It was found that a more protective layer is formed by magnetite than by iron carbonate.

The addition of 0.1 M $FeSO_4$ in groundwater (Smart et al., 2001) resulted in notably increased long-term hydrogen evolution rates, compared to KBS TR 36 groundwater. This was explained by the fact that non-protective layer of $FeSO_4$ might be formed on the surface of the carbon steel wires and prevented adherence of protective magnetite layer or alternatively iron sulphate may have caused iron carbonate to precipitate out of the solution, thus leading to a decrease in the pH and formation of a more aggressive environment. Only slight increase of hydrogen evolution was, however, observed with addition of K_2SO_4. An increase of hydrogen evolution by addition of $FeSO_4$ could be also explained by reactions of ferrous ions with water leading to hydrogen evolution. This reaction could also explain a significant decrease of pH observed under an addition of $FeSO_4$ to the groundwater. An increased acidity itself can also lead to increasing corrosion rate and hydrogen evolution.

The effect of ionic strength and addition of radiolysis products (9 mM NH_3 or 3 mM HNO_3) or of bentonite to groundwater was also investigated in the paper of Smart et al. (2001). It was observed that ionic strength caused a decrease in the hydrogen production during the first 500 hours compared to more dilute solutions, but in the long term (> 1000 hours) the corrosion rate was approximately an order of magnitude greater than in dilute groundwater. A number of explanations of this effect were formulated in the publication of Smart et al. (2001):

- Increased competition between the formation of magnetite and other less protective iron salts, such as $FeCO_3$ or $FeSO_4$.
- Increased availability of anions to form more soluble corrosion products, for example $FeCl_2$ instead of $Fe(OH)_2$, and hence reduced ability to form a protective magnetite film
- Incorporation of ions in the magnetite film increasing its conductivity
- Local buffering of pH
- Decrease in the thickness of the protective hard inner magnetite layer due to local buffering of the pH.
- Increased conductivity may enable more efficient electron transfer to occur between the carbon steel and the water.

The effect of an addition of 9 mM NH_3 or 3 mM HNO_3 was not significant. They also found that the corrosion rate of cast iron compared to carbon steel is lower. The gas generation rate did not increase significantly after removal of the non-adherent corrosion product, suggesting that hard not-removable inner layer provides the majority of the protection.

Honda et al. (1991) measured the corrosion rate of carbon steel in contact with compacted bentonite. Three specimens with compacted bentonite were placed in a teflon container and filled with water. The bentonite swelled and filled the container. An average corrosion rate was evaluated from the weight loss of specimens. The averaged corrosion rate decreased gradually with increasing test time and was estimated to be in the range 1 to 10 μm/year (0.2 – 2 $molm^{-2}yr^{-1}$) after period 180 days. Corrosion rates in compacted bentonite were approximately one order of magnitude lower than that in bentonite slurry. Corrosion rates in compacted bentonite mixed with synthetic sea-water were about 2 to 4 times higher than that in compacted bentonite mixed with distilled water. Corrosion rates in compacted bentonite mixed with distilled water were independent of the bentonite bulk density. On the other hand, corrosion rate in the compacted bentonite mixed with synthetic sea-water decreased with an increase in bulk density of the bentonite. Authors suppose that corrosion rates of carbon steel in compacted bentonite were controlled by the diffusion of dissolved oxygen in the compacted bentonite. Only magnetite was found in the case of tests with distilled water and siderite was identified on most of the specimens immersed in the compacted bentonite mixed with synthetic sea-water.

Kozaki et al. (1994) performed corrosion experiments of an iron foil activated by neutrons. The iron foil was placed between two water saturated bentonite specimens and allowed to corrode at 30 °C for periods 16 to 63 days. The corrosion rate was determined from measuring of total activity of ^{59}Fe released from the foil. No localized corrosion was observed on the surface of the foil. In all the experiments, the values of the corrosion rates in compacted bentonite were on the order of 1 μm $year^{-1}$, and no tendency to decrease in the corrosion rates was observed during the period of 60 days.

Anantamula et al. (1987) measured corrosion rate of carbon steel in the packing mixture of 75 wt% of basalt + 25 wt% of bentonite in water containing only 0.1 mg/l of oxygen at 150 °C. The corrosion rates achieved were in the range 23 – 28 μm/year for 1 week experiments and 11 – 14 μm/year for 2 week experiments. These values were at least 7 times lower than corrosion rates of the same types of steel in oxic conditions (95-230 μm/year).

Xia et al, 2005 performed anaerobic corrosion experiments on carbon steel in contact with compacted bentonite Kunigel V1 of different densities with samples pre-corroded under aerobic conditions. The corrosion rate observed was about 0.1 μm/year.

de Combarieu et al., 2007 has been performed recently corrosion experiments with iron powder. They found that the corrosion rate of iron powder under anaerobic condition in the presence of bentonite in solution was about 1.4 μm/year contrary to 0.66 μm/year without bentonite.

1.1.3 Conclusions

It follows from this literature review that hydrogen evolution from anaerobic corrosion of iron metals is not a constant value. A very high value about 20 $molm^{-2}yr^{-1}$ can be achieved at the beginning of corrosion until a corrosion layer is formed on the surface of metal. This depends strongly on the conditions of experiments such as: temperature, ionic strength, pH of water, or concentration of oxygen in groundwater. It follows from the results that after some time corrosion rate will decrease to much lower values, certainly below 5 μm/yr corresponding to hydrogen evolution rate lower than 1 $molm^{-2}$ yr^{-1}. Most of the experimental results, even suggest that corrosion rate in steady state in anaerobic conditions could be well below 1 or even 0.1 μm/yr (0.02 – 0,2 $molm^{-2}yr^{-1}$). The experiments reviewed however, have not been carried out in strictly defined conditions concerning the content of oxygen in water. The results can be doubted therefore from the point that corrosion layers formed on the surface of metal could be more protective than the corrosion layers formed in a repository conditions due to higher content of oxygen in groundwater.

Currently in NRI experiments of carbon steel under in anaerobic box with content of oxygen well below 0.1 ppm at various temperatures are under way. Eh, pH and hydrogen evolution is measured. Other experiments are focused on corrosion of iron powder in contact with compacted, saturated bentonite and also on migration of hydrogen through bentonite. We hope that the results can contribute to explaining some discrepancies observed in literature and provide more reliable data for performance assessments.

1.1.4 Literature

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1.2 CORROSION UNDER IRRADIATION

In geological repository, containers will be exposed simultaneously to water and radiation. Like corrosion processes, water decomposition under radiation will generate gases like hydrogen, oxygen and hydrogen peroxide. The aim of the study of this second part is to evaluate the impact of radiations on the corrosion processes of carbon steel.

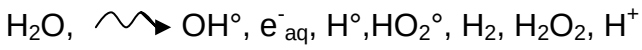
The second part of the progress report is devoted to the state of the art of radiolysis of solutions and of corrosion under radiation.

1.2.1 Radiolysis of solutions

Because of radioactive environment, radiolysis of water will occur and produces both radicals and molecular products which could accelerate the corrosion process.

1.2.1.1 PURE WATER RADIOLYSIS

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



$$H_2O, \rightsquigarrow OH°, e^-_{aq}, H°, HO_2°, H_2, H_2O_2, H^+$$

Where species noted ° are radicals and e^-_{aq} corresponds to a solvated electron.

The Linear Energy Transfer (LET), corresponding to the loss of energy by unit length in the medium, depends on the type and energy of the ionizing particles. The LET of high energy photons (such as gamma rays) is 0.2 keV per micrometer, while for alpha particle the LET can reach 200 keV/µm ((Pastina, 1999).

The yield of production for each of these species (primary products of radiolysis) depends on nature and intensity of the radiation (Pastina, 1999; Wasselin-Trupin, 2000) (Table 3).

Radiation	G(-H2O)	G(e-)	G(OH°)	G(H°)	G(H2)	G(H2O2)	G(H2O)
Gamma rays	1.08	2.63	2.72	0.55	0.45	0.68	0.008
Alpha rays	3.9	0.33	0.3	0.1	1.8	1.67	0.13

Table 3: Yields of primary species (Pastina, 1997)

Under continuous radiation conditions, the concentrations of radiolysis products depend on LET values. For high LET values, radicals yields are low and molecular species yields are high (Allen, 1961), while for low LET, radicals are preferentially formed.

The primary products undergo reactions (Ershov, 2008) with each other resulting in steady-state concentrations of both radicals and molecular species depending on dose rate, temperature and solution composition.

When irradiated with low LET, such as X-rays or gamma rays, pure degassed water gives almost no products (because of radical recombinations, water is formed), the amount of which of them remains at a very low steady state concentration. For high LET such as alpha rays, pure water decomposition occurs with the formation of hydrogen, hydrogen peroxide and molecular hydrogen. When water contains

oxygen, decomposition occurs whatever the LET value. If hydrogen is present in pure water, the water decomposition is suppressed. This behaviour is linked to the series of reactions involved in the chain reaction proposed by Allen (Allen, 1961) which can be summarized as:

$$OH^\circ + H_2 \rightarrow H^\circ + H_2O$$
$$H^\circ + H_2O_2 \rightarrow OH^\circ + H_2O$$
$$\text{----------}$$
$$H_2 + H_2O_2 \rightarrow 2\ H_2O$$

1.2.1.2 RADIOLYSIS PRODUCTS PROPERTIES

Some radiolysis products have acido-basic properties (H°, OH°, H_2O_2, HO_2°). Their acidity constants have been determined and gathered in Table 4.

equilibrium	pKa – 30°C
$H_2O = H^+ + OH^-$	13.85
$HO_2^\circ = O_2^{-} + H^+$	4.8
$H_2O_2 = HO_2^- + H^+$	11.62
$OH^\circ = O^- + H^+$	11.62
$H^\circ = e^-_{aq} + H+$	9.6

Table 4: Acido-basic equilibria (Elliot, 1994)

The radiolysis products range from oxidizing (OH°, H_2O_2, $O_2^{\circ-}$, HO_2° and O_2) to reducing (e^-_{aq}, H° and H_2) (Nielsen and Jonsson, 2008). These species, even at low concentrations, may determine the aqueous redox conditions strongly influencing corrosion kinetics (Pastina, 1999).

Redox reactions	Potential /ENH	Medium	References
$OH^\circ + e^-_{aq} + H^+ = H_2O$	2.72 V	In acidic conditions	(Spotheim-Maurizot et al., 2008)
$OH^\circ + e^-_{aq} = OH^-$	1.9 V	In neutral conditions	(Spotheim-Maurizot et al., 2008)
$e^-_{aq} + H+ = H^\circ$	- 2.31 V	In acidic conditions	(Pastina, 1997)

Table 5: Redox properties of some radiolysis products

1.2.1.3 INFLUENCE OF EXPERIMENTAL CONDITIONS

The steady state concentration of a radiolysis product will depend on its radiolysis production rate (constant at a constant dose rate) and on chemical decomposition rates which are very sensitive to aqueous environments such as pH, temperature and chemical additives (Buxton, 1988). Once generated, the primary products undergo further chemical reactions with each other and also with water molecules

and other chemical species present in solution (such as pH- or redox-controlling agents). Therefore, the solution chemistry would change with time (Lapuerta, 2007). The presence of dissolved species or a change in chemical environment affects the concentration of H_2O_2 and H_2 mainly through interactions with radicals e^-_{aq} and OH° (Ross, 1979).

a Dose rate

In the beginning of the exposure, the amount of radicals increases with radiation dose rate. But, because of the differences in kinetics of recombination reactions (Ross, 1994), a high dose rate induces an increase of molecular products, a decrease of radicals amounts and finally should conduct to water decomposition. Joseph et al. (Joseph, 2008) have shown that for a given pH the steady-state concentrations have a square root dependence on dose rate.

b Temperature

The diffusion in solution of primary radiolysis product is enhanced by temperature. Therefore, for high temperature the amount of radicals is high because of limited recombination reactions.

c Solution composition

If the water contains a few ppm of dissolved oxygen, the reducing species e^-_{aq}, H°, are rapidly converted to HO_2° and O_2^- respectively. In the case of oxygenated water, the concentrations of H_2 and H° decreased and the most abundant species are O_2 and H_2O_2. The presence of dissolved O_2 while radiation fields endures, will lead to a significant increase in the production of radiolytic oxidant. At pH 6, and a dose rate of 25Gy/s (gamma rays), the steady-state concentration of H_2 and H_2O_2 in aerated solutions reached 2.6 10^{-5}mol/l while it remains below the detection limit level in deaerated solutions The concentration of H_2O_2 was also below the detection limit in deaerated solutions whereas, in aerated solutions, this concentration quickly reached a steady-state concentration of 0.9 10^{-4}mol/l(Joseph, 2008).

The steady-state concentrations of water decomposition products are nearly independent of pH in the range 5-8. However raising pH above 10 significantly increases [H_2O] and [H_2] at the expenses of [OH°] and [e^-_{aq}]. The concentration of hydrogen peroxide after 5h irradiation (2.5Gy/s) was closed to 3.10^{-5} mol/l and those of hydrogen was 2.10^{-4} mol/l (Joseph, 2008; Yakabuskie, 2010). At pH>10, the production of oxygen becomes significant but at a finite rate.

When carbonate is present, as in bentonite porewater (Table 1), OH° will be quantitatively converted into CO_3^-°, this being also a strong oxidant (E_0 (NHE) = 1.9V and 1.59V respectively) (Nielsen, 2008). Fattahi et al (Fattahi et al., 1992) have reported an increase (factor 2) of hydrogen peroxide production for clay solution compared to pure water.

1.2.2 Radiolysis modelling

Modelling of radiolysis processes can be obtained with different codes. CHEMSIMUL is a computer program system for simulation of chemical kinetics (Rasmussen, 1984) is useful for the simulation of radiolysis processes.

Kinetics constant rates laws are obtained in RATES data base (Ross, 1994) and completed by literature review (Buxton, 1988; Ershov, 2008). An example of input data is given in annex 2.

An illustration of the capabilities of this code is given on figures 3 and 4. In pure deaerated water, the production of hydrogen increases with the dose rate and the duration of radiation (total dose). Fig. 4 shows the differences of hydrogen production under radiation for two solutions: pure water and solution containing carbonate.

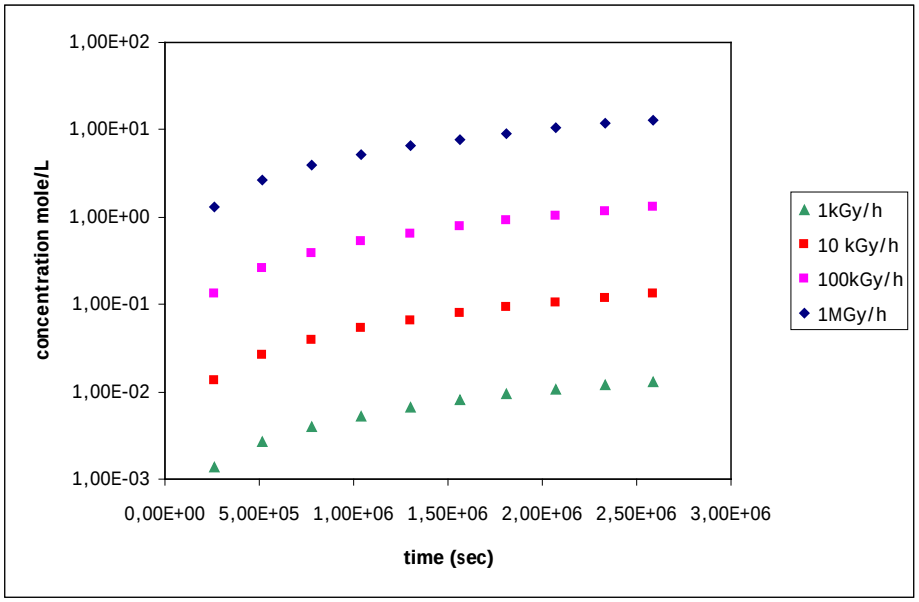


Figure 3: Hydrogen production by irradiated water as a function of dose rate

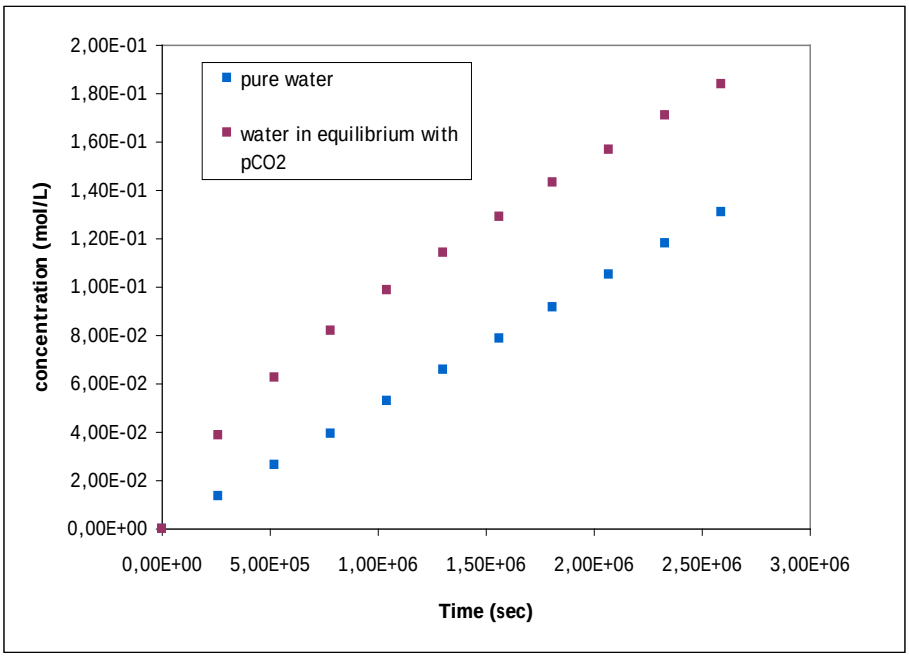


Figure 4: Influence of carbonate on hydrogen production – dose rate = 10kGy/h

1.2.3 Influence of radiation on corrosion

The overall redox conditions are established by interactions between reactive radiolysis products, the steel surface and corrosion products produced by these reactions (Joseph, 2008).

Numerous oxidizing and reducing products are produced, all of which can affect the oxidation potential and carbon steel corrosion (Fig. 5).

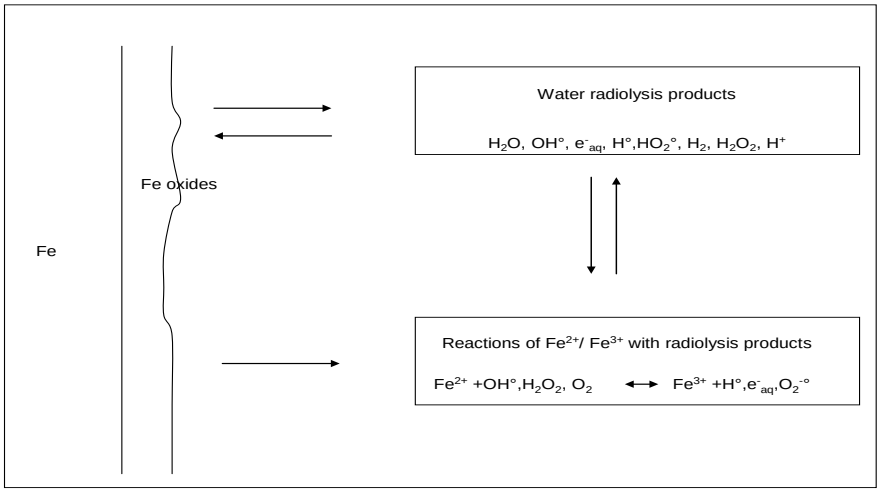


Figure 5: An example of reactions occurring at the interface of carbon steel solution under irradiation (from(Zhang et al., 2007)).

Several papers have put in evidence enhanced corrosion of different materials under charged particle radiations; ceramics, zircaloy and other metals (Burns, 1983; Ishigure, 1980; Lapuerta et al., 2005; Lillard, 2000).

The influence of ionizing radiation on corrosion of metals has been studied only to a limited extent, and the mechanism by which the radiation affects corrosion kinetics has not been established (Daub 2009). The observed effects of ionizing radiation on the corrosion of metals are conflicting and many key questions remain unanswered.

Literature reports some studies on the corrosion processes in primary coolant water of nuclear power plants (Daub, 2008; Pastina, 1999). To limit the corrosion processes in primary coolant water in nuclear reactors, an excess of molecular hydrogen is dissolved in this water. Molecular hydrogen will prevent the accumulation of oxidants products such as oxygen and hydrogen peroxide, which are responsible for the corrosion of the primary system (Pastina, 1999). The molecular hydrogen participates to a chain reaction which recombines H, OH and H_2O_2 back to water (Allen chain).

An experimental study (Marsh et al. 1988) on the corrosion of carbon steel in presence and absence of radiation (dose rate up to 10^2 rad/h) has been conducted in synthetic granitic waters (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 10^5rad/h, the general corrosion rate was fairly constant at 3 µm/y at least up to 5236 h (duration of the experiment). As on unirradiated samples, no localized corrosion was observed.

More recently, Daub (Daub, 2009) have shown that the corrosion behaviour for a pH of 10.6 under gamma-irradiation at room temperature could be simulated well by exposing the steel to solutions containing an equivalent concentration of hydrogen peroxide. More, these authors observed that the addition of H_2O_2 in multiple steps matches the change in corrosion potential under irradiation. In the conditions of the experiment, Daub (2009) concludes that H_2O_2 is the key radiolysis product.

Lapuerta et al. (Lapuerta et al., 2005; Lapuerta, 2007; Lapuerta, 2006) have studied corrosion of iron under proton radiation in atmospheric conditions and in aqueous medium.

In atmosphere, without radiation, the corrosion kinetics is maximum for a relative humidity of 80-90%. Under radiation, the maximum of corrosion is observed for a humidity of 45%. For higher humidity content, the corrosion rate decreases. The results show that radiation influences corrosion only when water (vapour) and oxygen are simultaneously present.

As in atmospheric conditions, under radiation, iron corrosion in solution is enhanced when oxygen is present (corrosion is twice more significant in aerated medium than in deaerated one). Moreover, Lapuerta et al. (Lapuerta, 2007) has shown that the radicals produced by water radiolysis participate to the corrosion processes (together with hydrogen peroxide).

Smart et al. (Smart, 2008) have conducted experiments designed to investigate the effect of gamma radiation on the corrosion of steel in repository environments.

Tests were carried out, in anaerobic environments, on carbon steel wires for 2 temperatures (30°C and 50°C), 2 dose rates (11Gy/h, 300 Gy/h) in 2 different artificial groundwaters (Modified Allard GW, bentonite equilibrated GW).

Radiation was found to enhance the corrosion rates at both dose rates but the greatest enhancement occurred at the higher dose rate. The presence of gamma radiation increases the anaerobic corrosion of carbon steel in artificial groundwaters. At 11Gy/h, the increases only lasts for 7 000 hours, but at 300Gy/h, the enhancement is longer lasting. The enhancement of the corrosion rate is higher in "Allard water" where a 30 fold increase was observed than in "bentonite water" which has a higher ionic strength and a higher initial pH, where the radiation-induced enhancement was 10-20 times. The corrosion rate value estimated on the basis of hydrogen release is closed to values obtained by Marsh and Taylor (3 µm/y compared to less than 0.1µm/year without radiation). No localised attack was observed.

The variation of pH of solutions after irradiation experiments is less than 0.1 (Marsh and Taylor, 1988; Smart, 2008).

Fujita et al. (Fujita et al., 2000; Fujita et al., 2001) have observed a corrosion rate in pure deaerated water under a dose rate of 0.55kGy/h for 300, 600 and 900h six times larger as that under a non-irradiated condition.

The main corrosion product is magnetite, Fe_3O_4, but there was some evidence of higher oxidation state oxy hydroxides (Fe_2O_3, FeOOH) under high dose rate (Daub, 2009; Xu et al., 2008).

Smart (Smart, 2008) mentioned that the corrosion product formed under high dose rate (300Gy/h) has a different colour to the specimen obtained at 0 and 11Gy/h. Fujita et al. 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.

1.2.4 Conclusion

Studies devoted to the corrosion of iron under radiation seem indicate that the corrosion of carbon steel is enhanced under irradiation. But uncertainties still remain about the factor of enhancement. Most of these studies are conducted in pure water and the influence of dissolved species on corrosion under species is not currently studied. Generally, authors have observed the formation at the interface steel/solution of magnetite together with oxy-hydroxide. It is necessary to examine the influence of this last oxide on the corrosion rate.

At least, no unanimity was obtained towards the state of the surface of carbon steel corroded under irradiation. Is it a generalized or localized corrosion (cracks)?

The experimental program developed will bring some answer to those questions.

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Annexes

Table 1: Composition of clay porewater for 3 different dry densities

Dry density (kg/cm3)	1300	1600	1900
Porosity	0.122	0.044	0.019
Log PCO_2	- 3.42	-3.47	-3.65
Na (M)	0.183	0.207	0.254
K (M)	0.0027	0.0031	0.0037
Mg (M)	0.01	0.012	0.015
Ca (M)	0.0092	0.0098	0.012
Sr (M)	8.1 E-5	8.6 E-5	1.1 E-4
Cl (M)	0.0181	0.0618	0.17
SO4 (M)	0.102	0.095	0.071
Cinorg (M)	8.9 E-4	8 E-4	5.5 E-4
F (M)	2.2 E-4	2.2 E-4	1.9 E-4
Si (M)	1.8 E-4	1.8 E-4	1.8 E-4

CHEMSIMUL: .dat

$chemical reactions

* équilibres acide base
*H20 !pke=15.75 !molecule d'eau=55.5
RE1: H2O+H2O=OH[-]+H3O[+]; A=2.36e-5
RE2: OH[-]+H3O[+]=H2O+H2O; A=1.3e11
...
* reactions with e-aq
RE15: E[-]+E[-]=H2+OH[-]+OH[-]; A=5.5E9
RE16: E[-]+H=H2+OH[-]; A=2.54E10
..

*reactions with radical H
RE25: H + O[-] = OH[-] ; A=1E10
...

* reactions with radical OH
RE33: OH+H2=H2O+H; A=6e7
RE34: OH + OH = H2O2 ; A=5.5E9
.....

* reactions with radical HO2
RE40: HO2+O2[-]=HO2[-]+O2; A=9.7e7
RE41: HO2+HO2=H2O2+O2; A=8.3e5

* reactions with radical O[-]
RE42: O[-] + H2 = H + OH[-] ; A=1.E8
...

* reactions with radical O3[-]
RE50: O3[-] = O2 + O[-] ; A=2.6E3
....

* reactions with carbonates
RE63: HCO3[-]+OH=CO3[-]+H20; A=8.5e6
...

* reactions with .... Solution species (sulfate, nitrate..)

Solution composition

$concentrations déduites de Jchess eau-oxygene
con(H3O[+])=0
con(HCO3[-])=2.2e-6
con(H2CO3)=1.0735e-5
con(H20)=55.5e0
con(OH[-])=0
con(O2)=2.52e-4
con(CO3[--])=4.71e-11

$integration

eps=1.0e-5
*fststp=5.0e-7
*hmax=5.0e-3
tend=1.296e6
*jt=

$output control

*derivative(O2)
dig=3
mathinfo
diffeq
linele=80
prints=110
radprs=110
*printonly(H2O2,H2)
*save

$irradiation

G(H)=0.5
G(OH)=1
G(H2O2)=1.2
G(E[-])=0.74
G(H2)=0.88
G(H3O[+])=0.74
G(HO2)=0.2
G(H2O)=-4.54
*nrr
RADTIME=1.296e6
*ttrain
TOTALDOSE=1.26e6