EPJ Web of Conferences **56**, 05002 (2013)
DOI: 10.1051/epjconf/20135605002

Modelling of hydrogen production from pore water radiolysis in cemented intermediate level waste

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Abstract. In France, some of the intermediate and low level wastes are embedded in hydraulic binder and put into concrete canisters. They contain β and γ emitters which cause an irradiation of water present in the pores of the hydraulic binder. This is responsible for a dihydrogen (H_2) production due to radiolysis. EDF R&D and CEA have collaborated since many years in order to understand this phenomenon and develop a model called DO-RE-MI which can predict such a production of dihydrogen in concrete waste packages. A parametric study, using the developed model, was implemented in order to determine the effects of each parameter on H_2 production. The main results are presented in this paper.

1 Introduction

In France, some of the intermediate and low level wastes are embedded in hydraulic binder and put into concrete canisters. For EDF, the wastes concerned by this packaging are control rods of pressurized water reactor (ILW) and decommissioning activated wastes of first generation reactors (mainly LLW). They contain β and γ emitters which causes a self-irradiation of hydraulic binder and concrete.

The water present in the pores of the hydraulic binder, subject to the waste irradiation, is responsible for a dihydrogen (H_2) production due to radiolysis. This production is a function of different parameters:

- water saturation,
- dose rate,
- presence of iron species in pore water,
- cement porosity.

EDF R&D and CEA have collaborated since many years in order to understand this phenomenon and develop a model called DO-RE-MI (Description Opérationnelle de la Radiolyse de l'Eau dans les Matériaux Irradiés) which can predict such a production of dihydrogen in concrete waste packages [1].

A parametric study, using the developed model, was implemented in order to determine the effects of each parameter. The calculations were made using a homogenous dose rate throughout the hydraulic binder. For a real case, the dose rate should be evaluated as a function of hydraulic binder

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geometry and waste type, using an adapted computer code (e.g. TRIPOLI). The main results are presented in this paper.

2 Description of the model and hypothesis of the study

2.1 Radiolysis model description

A model, called DO-RE-MI, has been developed by CEA for the estimation of the H_2 source term generated by γ irradiated cement-based materials [1]. It consists in simulating the radiolysis of the pore liquid with elementary reactions relating to the decomposition of alkaline water.

The production of gaseous H_2 by cement-based materials exposed directly or indirectly to ionising radiation results from the radiolysis of the residual water occupying part of the porosity of such materials. More specifically, it should be worded as the radiolysis of the H_2O solvent within an alkaline solution with a pH being often quite higher than 13, in equilibrium with the hydrated minerals of the concrete and more particularly with $Ca(OH)_2$ (portlandite). Usually, the pH is equal to 12.4, a pH of 13 and above is due to NaOH and KOH presence. In the framework of that simplified chemical description, the review of the radiolytic mechanisms highlights an Allen-type reaction chain, similar to the known one of neutral pH [2], but characterised by faster kinetics [3]. Hence, at a pH higher than 13, the "classic" chain-reaction (generic writing with convention $e^-_{aq} = H_2O^-$):

$$OH^\bullet + H_2 \rightarrow H^\bullet + H_2O \qquad k = 4.2\times10^7\ M^{-1}\cdot s^{-1} \tag{1}$$

$$H^\bullet + H_2O_2 \rightarrow OH^\bullet + H_2O \qquad k = 3.6\times10^7\ M^{-1}\cdot s^{-1} \tag{2}$$

becomes:

$$O^{\bullet-} + H_2 \rightarrow e^-_{aq} \qquad k = 1.2\times10^8\ M^{-1}\cdot s^{-1} \tag{3}$$

$$e^-_{aq} + HO_2^- \rightarrow O^{\bullet-} + OH^- + H_2O \qquad k = 3.5\times10^9\ M^{-1}\cdot s^{-1} \tag{4}$$

The consequence of a faster rate in the new reaction chain is a better efficiency in the destruction of H_2 in an alkaline environment, which constitutes an interesting result from an operational standpoint (e.g., reduction in the quantity of gases emitted within disposal sites for cemented radioactive-waste). Moreover, it induces an efficient recycling of radiolytic H_2 in closed systems, such as concrete pores filled with water.

The model has been upgraded recently in order to take into account the influence of impurities contained in the cement which may influence the production of H_2. Iron, which is systematically present in cement materials, is the main impurity likely to influence radiolysis. The issue of iron in the radiolysis of cement media refers primarily to the disturbance induced by that element on radical chemistry throughout the irradiation period. Reactivity of e_{aq}^- and $OH^\bullet$ radicals is faster on Fe(III) and Fe(II), respectively, than on the H_2O_2 and H_2, which are primary radiolytic products in the “Allen’s chain-reaction”.

$$O^{\bullet-} + Fe(II) \rightarrow O^{2-} + Fe(III) \qquad k \approx 10^8 - 10^9\ M^{-1}\cdot s^{-1} \tag{5}$$

$$e^-_{aq} + Fe(III) \rightarrow H_2O + Fe(II) \qquad k \approx 10^{10}\ M^{-1}\cdot s^{-1} \tag{6}$$

Under those conditions, the survival rate of H_2 in solution is higher since the attack of radical $O^{\bullet-}$ aims preferentially at Fe(II) and not at H_2.

A critical review of the iron chemistry under radiation from literature data and an implementation of the water radiolysis model in the presence of iron has been published in 2009 [4]. Such coupling phenomena between radiolysis chemistry and gaseous transport only concern β/γ emitters and not α emitters which do not produce enough oxidant radicals to lead to a H_2 recycling.

2.2 Test cases definition

The parametric study has been performed for a theoretical cylindrical concrete waste package (Figure 1). We consider that wastes and hydraulic binder would be placed in an inner steel basket which remains open on the top face (closure is performed by a concrete cover). The production of gaseous H_2 results from the radiolysis of the residual water occupying part of the porosity of hydraulic binder. As a consequence, diffusion process and hydrogen exit from the package only occur in one direction, through the top face. Therefore, calculations are made on 1D, over the inner height of the container (1 m).

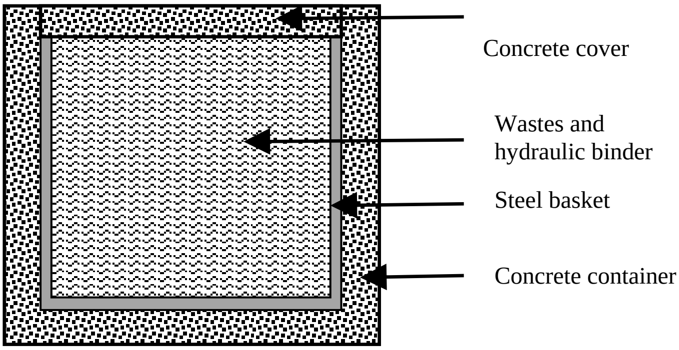

Fig. 1. Schematic representation of the concrete package.

Three hydraulic binder porosities are chosen for the study: 0.44, 0.55 and 0.65. When porosity increases, water content and gas diffusion in the binder increases too. Evolution of those two parameters with porosity is automatically taken into account in the model. The hydraulic binder weight in the container is 1000 kg.
Irradiation comes from a ^{60}Co source which is assumed to be homogenised in the hydraulic binder. As a reference for our calculations, we choose an initial irradiation dose rate received by the pore water of 165 Gy/h. In order to test the influence of dose rate, an increased value has also been tested (255 Gy/h). Both dose rates are very high and are upper values of the most irradiating ILW that may be embedded in such waste packages.
Calculations have been made at 20°C. In most cases, results are presented as the cumulated quantity of hydrogen (arbitrary unit: a.u.) produced in the container over 100 years.

3 Results

3.1 Influence of hydraulic binder water content

The dihydrogen production as a function of water saturation has been calculated in the reference case: 0.44 binder porosity, no iron content, dose rate of 165 Gy/h. It follows the trend shown in Figure 2, a shaped-bell curve with a maximum near a water saturation of 64%.

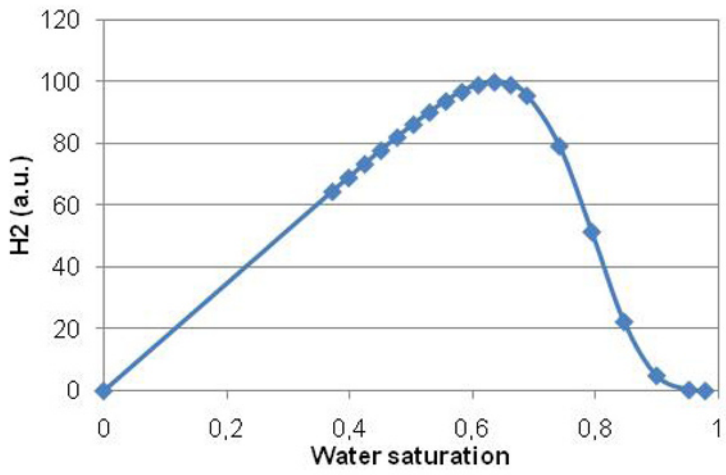

Fig. 2. Dihydrogen production over 100 years as a function of saturation index.

The influence of water content can be understood as follow:

- For saturation indexes below 0.6, H_2 production increases as water saturation rises. The production is almost proportional to the water saturation. Indeed, with such low water content, a high fraction of the porosity is open to gases. Hence, dihydrogen produced by water radiolysis can easily move to the gas phase. Then it is not available anymore for recombination with other oxidant species formed in the liquid phase, and it will migrate in the binder by gaseous diffusion which is fairly rapid in high porosity materials such as hydraulic binders. Therefore, in these conditions, almost all the dihydrogen produced move outside the container (recycling is negligible) and the production of hydrogen is proportional to the quantity of water available in the binder for radiolysis.
- For saturation indexes between 0.6 and 0.67, the dihydrogen reaches a maximum due to a change in the gas diffusion regime: porosity open to gases starts to decrease and the time of residence of dihydrogen in water rises leading to a significant recycling with radiolytic oxidant species.
- For saturation indexes between 0.67 and 0.9, the dihydrogen production sharply decreases. In these conditions, the fraction of gas in porosity strongly decreases which leads to fall of the hydrogen diffusion coefficient up to 4 orders of magnitude [5] (Figure 3). As a consequence, the radiolytic recycling efficiency rises. The higher the water content, the better the recycling and the less the dihydrogen production.
- For saturation indexes greater than 0.9, dihydrogen production becomes very low in the neighbourhood of the complete water saturation. In that case, almost all the hydrogen stays in the water and is recycled.

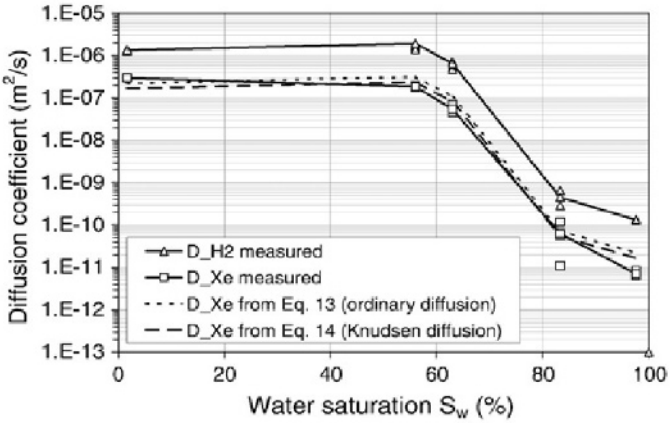

Fig. 3: Dihydrogen and xenon diffusion in hydraulic binders [5].

3.2 Influence of dose rate

The influence of dose rate on dihydrogen production has been calculated in the reference case (binder porosity = 0.44, no iron content) for two dose rates: 165 Gy/h and 255 Gy/h. Results are presented in Figure 4. As expected, the results show that the higher the dose, the higher the H_2 production. Nevertheless, at high saturation the H_2 production is independent from the dose rate.

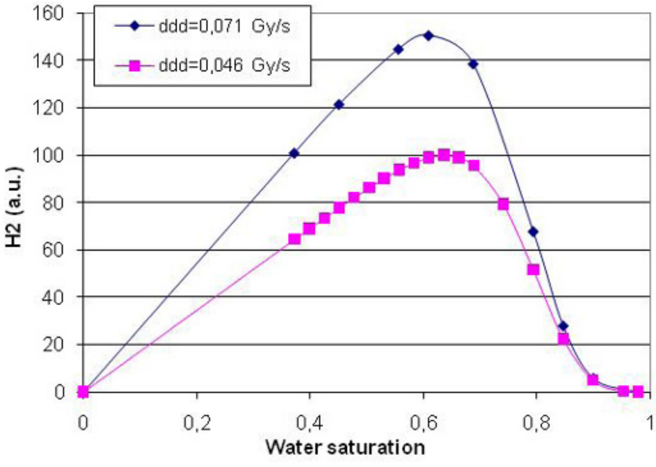

Fig. 4: Dihydrogen production over 100 years vs. water saturation, as a function of γ irradiation dose rate.

3.3 Influence of iron

The influence of iron (present in concrete as FeOOH) has been evaluated by comparison with the reference case (porosity = 0.44, dose rate = 165 kG/h). As shown in Figure 5, the coupling between gas transfer and chemistry in solution is modified by the presence of Fe aqueous species, particularly beyond a saturation index of 0.6 from which amounts of produced H_2 are higher.

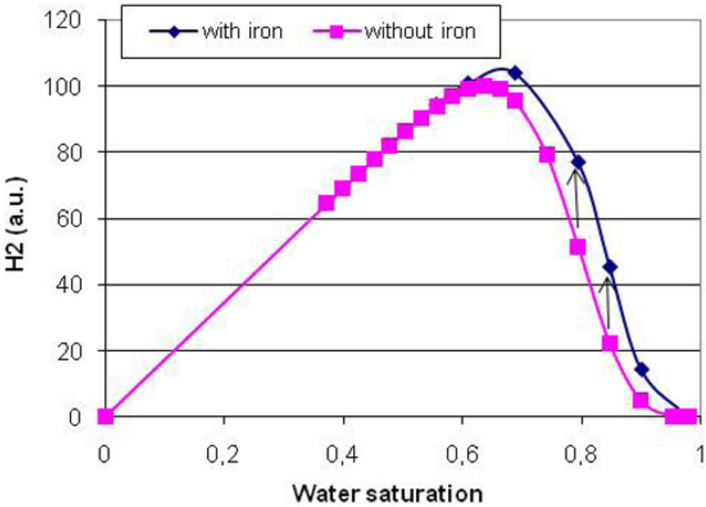

Fig. 5: Dihydrogen production for 100 years as a function of saturation, in the presence and absence of iron.

At low saturation, gas transfer prevails and dihydrogen moves easily from the liquid phase to the gas phase. Therefore, in both cases (with or without iron), the efficiency of radiolytic recycling is very low and iron has no significant effect.

At high saturation (beyond 0.6), where a significant recycling of dihydrogen occurs in absence of iron due to high residence time of H_2 in solution, the H_2 chemical recombination is disturbed by redox reactions between radicals (e_{aq}^-, O^-) and iron solutes (Fe(III), Fe(II)). The influence of iron on dihydrogen production is very significative on this range of water saturation (it can reach 100% increase for saturation close to 0.9). Nevertheless, the effect on the peak value (at w~0.64) is low, only few percent increase. It is the consequence of the strong effect of water saturation on the gas phase diffusion which decreases sharply in all cases and has a higher effect than iron.

3.4 Influence of cement porosity

The influence of the hydraulic binder porosity has been also tested. The tested porosities correspond to very porous materials, the higher value is probably not realistic in terms of binder fabrication. Results are presented in Figure 6. The higher the porosity, the higher the hydrogen production. This behaviour can be explained by the same coupling “gas transfer - solution chemistry” insofar as high porosities lead to easier diffusion of H_2 (which cannot be recombined any more). The gradual increase in dihydrogen production is mainly due to the water content increase inside the binder which lead to higher radiolysis.

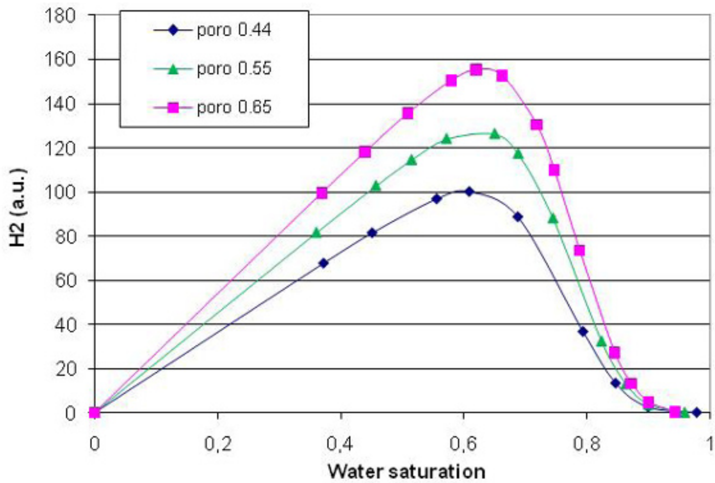

Fig. 6: Dihydrogen production for 100 years as a function of hydraulic binder porosity.

3.5 Evolution of dihydrogen production versus time

The evolution of the dihydrogen production versus time depends on the radioactive periods of the radionuclides contained in the wastes. For this study we have chosen a unique source of ^{60}Co responsible for the radiation dose. This choice has been made because ^{60}Co is one of the most intense γ emitter and is present in many activated ILW. Due to its relatively short period (5,3 years), the dihydrogen production rate is high during the first decades, but becomes negligible after 50 years (Figure 7). For a real waste package, the dose rate will be a combination of the different radionuclides half life, energies and concentration. Therefore, the radiolytic dihydrogen production may be slower at the early stages but may last longer.

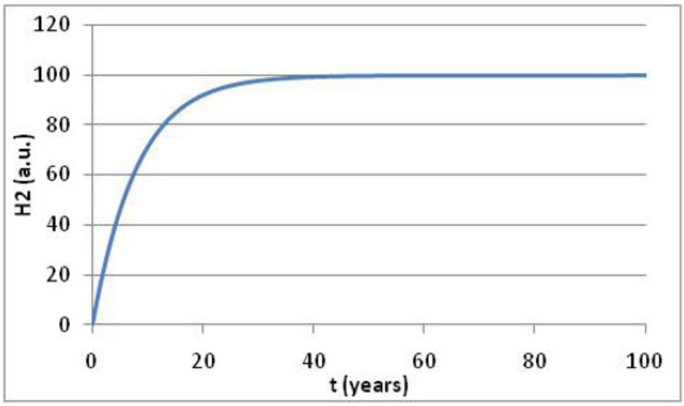

Fig. 7: Dihydrogen production vs. time (w = 0,64 ; porosity = 0,44 ; dose rate = 165 Gy/h).

4 Conclusions

The model (DO-RE-MI) developed by CEA to predict the production of dihydrogen due to water radiolysis in concrete waste packages has been applied to a theoretical package for a parametric study in order to determine the effects of the main parameters that may affect this phenomenon. The wastes contain β and γ emitters. The main results are the following:

- Radiolytic dihydrogen production is strongly dependent on the hydraulic binder water saturation. It follows a bell shape curve with a maximum production near 0.64 saturation. For lower saturation indexes, the hydrogen production is proportional to the binder water content since easy hydrogen gaseous diffusion allows complete gas exit and negligible radiolytic recycling. For higher saturation indexes, hydrogen production undergoes a sharp decrease due to strong decrease in gaseous diffusion in the binder. In such situation, radiolytic hydrogen recycling becomes very efficient, and, near complete water saturation, almost all the radiolytic hydrogen is recycled.
- Dose rate has a direct effect on radiolytic production of dihydrogen. The kinetic of production depends on the radionuclides periods present in the wastes. In the case of ^{60}Co chosen for this parametric study, all the hydrogen is produced during the first 50 years.
- The influence of iron species in pore water has been evaluated. Under those conditions, the survival rate of H_2 in solution may be higher since the attack of radical $O^{\bullet-}$ aims preferentially at Fe(II) and not at H_2. This is what we actually observe for water saturations greater than 0.64 where significant dihydrogen recycling has been observed in absence of iron. In this saturation region, presence of iron in the binder leads to an increase of the hydrogen production (up to +100%) for a given saturation index. On the opposite, no effect of iron is observed for lower saturation index due to the fact that in both cases (with or without iron), almost no hydrogen recycling occurs. Finally, we can observe that the effect of iron on the peak hydrogen production is very low (only few percents at 0.64 saturation index).
- Finally, the effect of hydraulic binder porosity has also been investigated. The higher the porosity, the higher the radiolytic dihydrogen production. This is mainly due to the direct increase of pore water content with the increasing binder porosity.

This study helps in understanding the behaviour of concrete packages used for nuclear wastes. Hydrogen production can then be estimated as a function of time and other parameters specific of the package conception, type of waste content and of the interim storage and disposal environmental conditions.

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