Contribution of the Tricalcium Silicate Hydration Products to the Formation of Radiolytic H₂: A Systemic Approach

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Abstract

Because they contain residual water, cementitious materials produce radiolytic dihydrogen under irradiation, which can pose a safety concern for some nuclear applications. The estimation of H₂ emissions by current models takes into account the contribution of pore water but not that of solid hydrates, which is considered negligible. Gamma irradiation (dose rate of 359 Gy h⁻¹ up to 6 months in a closed system under Ar gas) of hydrated tricalcium silicate pastes, the main constituent of Portland cement, shows however an initial contribution of solid hydrates to H₂ formation. A systemic study combining the source term of solid hydrates and the pore water radiolysis using simulation shows that the primary radiolytic yield devoted to portlandite and cementitious C-S-H (together) is of the order of 2.8 × 10⁻⁸ mol J⁻¹, and that the contribution of the solid phases is decreasing and becomes negligible in the long term, suggesting a saturation effect with dose. Even if limited in time, the additional H₂ source term is very sensitive on the radiolysis of the pore water with the very strong solicitation of the recycling reaction chain (equivalent to the Allen chain in basic medium) and leads to a frankly reducing medium (Eh ≈ −470 mV NHE).

1. Introduction

Among the solutions chosen for the conditioning of low- and medium-level radioactive wastes, cementitious materials play an important role due to their numerous advantages (diversity, low cost, ease of implementation). However, the introduction of α and β/γ-emitting wastes in contact with or near water present in the cementitious matrices can lead to radiolysis, and hence, to the formation of dihydrogen. The potential accumulation of this gas in the air around the cemented waste packages, in particular during the storage period, constitutes a safety problem for which the level of risk has to be assessed. This radiolysis problem also exists in concrete subjected to significant external irradiation (γ and neutron) in nuclear power plants (biological shield in the vicinity of a reactor vessel).

Generally, the evaluation of the emitted quantities of H₂ is based on the prior simulation of radiolysis within the cemented radwastes or radiation shielding concretes, taking into account a set of varied and coupled phenomena (radioactive decay, radiation chemistry, gas transport, heterogeneous equilibria gas-liquid-solid phases) (Bouniol 2004; Bouniol and Bjergbakke 2008). Since the first operational calculations (Christensen and Bjergbakke 1984; Offermann 1988), the main assumption on which this type of simulation has been based is that only the residual free water in the cementitious matrix is supposed to be affected by ionizing radiation, according to the known primary yields for bulk water [values depending only on temperature and pH for a given radiation (Elliot and Bartels 2009; Haïssinsky 1967; Hayon 1965)]. Under these conditions, the quantity of water used during the hydration of the cement for the constitution of the solid phases [where it appears in the form of constitution (OH⁻) or crystallization (H₂O) water], is completely neglected. However, the corresponding water amount can be significant. Thus, in a Portland cement paste with an initial water/cement mass ratio of 0.42 (minimum value for complete hydration) (Jensen and Hansen 2001), the water fraction used for the constitution of hydrates (bound water) represents approximately 55% of the total water, which is not negligible if this type of water would be affected by ionizing radiation.

Two solid phases are mainly produced upon hydration of Portland cement: portlandite [Ca(OH)₂] and cementitious calcium silicate hydrate ("C-S-H"). Portlandite contains only constitution water (OH⁻) within a compact crystalline structure (Aierken et al. 2015). For this mineral, a significant H₂ yield of 2.1 × 10⁻⁸ mol J⁻¹ was measured under gamma irradiation (LaVerne and Tandon 2005). Curiously, this yield seems closer to that of water (= 4.5 × 10⁻⁸ mol J⁻¹ at 25°C (Elliot and Bartels 2009)) than that determined for a similar hydroxide Mg(OH)₂, for which the dihydrogen radiolytic yields was reported to be 5.3 × 10⁻⁸ mol J⁻¹ under the same irradiation conditions (LaVerne and Tandon 2005). Cementitious calcium silicate hydrate contains water in three different forms (constitution, crystallization and adsorbed) in a mainly amorphous, non-stoichiometric and microporous "gel". Determining an H₂ yield for cementitious C-S-H alone is difficult because it strongly depends on the manufacturing protocol, the relative hu-
midity at which the material is equilibrated or the drying procedure. This is one reason why it is difficult to find typical experimental values in the literature. For instance, dihydrogen radiolytic yields ($\gamma$) were reported for synthetic C-S-Hs having Ca/Si ratios ranging between 0.8 and 1.4, stored and irradiated at 60% relative humidity (Yin et al. 2019). They were found to be between 6.1 and $3.6 \times 10^{-4}$ mol J$^{-1}$, respectively but the participation of adsorbed water in the production of radiolytic H$_2$ is therefore probable. Values between 3.1 and $7.3 \times 10^{-9}$ mol J$^{-1}$ were obtained under $\gamma$-irradiation of cement pastes heated to 120°C, but the material was a mixture of portlandite and cementitious C-S-H (Ishikawa et al. 2019). Furthermore, the temperature chosen to eliminate adsorbed water certainly affected part of the bound water in the last component. The overall production of H$_2$ by Portland cement pastes with or without the addition of ground quartz was also investigated under electron irradiation. (Le Caër et al. 2017). Globally, the apparent yield of H$_2$ was shown to increase with relative humidity, i.e., with the quantity of "free" water. For a material dehydrated at 110°C in order to remove "free" water, the H$_2$ yield was low, smaller than $5 \times 10^{-9}$ mol J$^{-1}$. Besides, DFT calculations suggested that, independently of the water content of the C-S-H considered, the radiolytic production of H$_2$ could be tuned by a structural effect. However, from a structural point of view, $^{29}$Si NMR examination of several cementitious C-S-H irradiated for one year with a current of 40 mA. Diffraction diagrams were obtained by considering the volume of the capillary connected to the dead space to a minimum (better sensitivity on the pressure response). The latter represents about 30 cm$^3$.

The determination of the rate of H$_2$ production for each hydrated cementitious phase (individually) appearing delicate, this work seeks to highlight by a systemic approach the existence of a primary production of H$_2$ for both solid phases of a hydrated Ca$_3$SiO$_5$ paste (simplified representation of a Portland type cementitious matrix with the same main hydration products) under gamma irradiation. The idea is to measure the amount of H$_2$ produced by the whole system like a previous study (Bouniol et al. 2013) and to obtain the contribution of the hydrated solid phases by subtracting that of the pore water, calculated separately, close to the initial time. In this approach and in a second step, simulation is an essential tool to evaluate the effect of an additional primary H$_2$ yield on the system behavior (coupling with pore water radiolysis) and to hypothesize the nature of the mechanisms.

2. Materials and methods

2.1 Material studied and preparation

Following an experiment conducted on industrial cements to show the chemical effect of sulfide on radiolysis (Bouniol et al. 2018), a new experiment was conducted with a neat paste of tricalcium silicate considered as a reference material. The paste was prepared in a glove box under argon from ground pure tricalcium silicate (triclinic variety provided by Mineral Research Processing (Meyzieu, France), specific surface of 0.3 m$^2$ g$^{-1}$ (Blaine method), density of 3120 kg m$^{-3}$), using a hydration solution with NaOH = 0.24 mol kg$^{-1}$ such that the H$_2$O/ Ca$_3$SiO$_5$ mass ratio is 0.4. This alkaline addition allows to obtain a pH higher than 13, representative of the hydrolysis conditions of tricalcium silicate in a Portland cement. The fresh material was introduced in three cylindrical glass containers, each receiving a volume of 111.45 cm$^3$. Samples were then kept for 72 hours in a climate cabinet at 100% relative humidity (to avoid desiccation during the curing phase) and then stored in a sealed bag under Ar gas. After 10 months of curing, the material was already mature, with complete hydration (no residual Ca$_3$SiO$_5$ verified by XRD). At the end of its hydration process, the material obtained is a mixture of cementitious C-S-H and portlandite in the proportions expected from the hydration reaction (see Section 4.1, Reaction R2).

2.2 XRD characterization

Mineralogical determinations were performed with a PANalytical X'Pert MPD PRO diffractometer with a "Bragg-Brentano" geometry 0-20 equipped with a X'celerator detector. The tube provides K$_\alpha$ radiation from a copper anticathode [K$_\alpha$(Cu) = 0.154 nm, K$_\alpha_2$ being filtered] and is operated with a voltage of 45 kV and a current of 40 mA. Diffraction diagrams were obtained at room temperature from grinded materials (grain size < 40 µm) using a sample spinner (rotation speed = 1 s$^{-1}$). Measurement conditions had a range of 20 from 4 to 70°, a step size of 0.01 degree with 60 s per step.

2.3 Irradiation and gas measurements

The Ca$_3$SiO$_5$ pastes were irradiated inside three cylindrical stainless steel (AISI 304) mini-containers with a useful volume of 325.9 cm$^3$ (Fig. 1). The internal diameter of 5.0 cm and the wall thickness of 3 mm minimize the dose gradients associated with external irradiation. Given the volume of Ca$_3$SiO$_5$ paste limited by glass walls, a 143.0 cm$^3$ metal wedge allows to reduce the dead space to a minimum (better sensitivity on the pressure response). The latter represents about 30 cm$^3$ by considering the volume of the capillary connected to the pressure sensor. The sealing of the mini-containers was achieved by means of a Helicoflex silver-plated gasket.

The three mini-containers planned for three irradiation times were disposed along an arc of circle, 72 cm from the center of a radiation source consisting of 9 rods of $^{60}$Co placed on a circular rack in the "Pagure" irradiator (CEA/Paris-Saclay). Their total initial activity (672.55 TBq) generates a dose rate in pore water equal to 359 ± 9 Gy h$^{-1}$. This value refers to initial KERMA (Kinetic Energy Released per unit MAss) rate computed for H and O atoms in water (on average in the material) when irradiation begins, using the "Tripoli-4" Monte-Carlo
Moreover, temperature and total pressure were measured continuously with a PT-100 probe and a Keller 0-10 bar sensor (accuracy of ±0.1%) respectively. The temperature was 21.2 ± 3.1°C on average over a period of 6 months.

The gas analysis in each mini-container was performed before irradiation (t₀), and then at the respective target time for each of them (i.e., 62, 132 and 195 days after t₀). The gases were measured with a high-resolution magnetic-field mass spectrometer (HRMS) that allowed identification and quantification of the gaseous compounds having a mass ranging from 2 to 200. The results obtained, with a precision of ±1%, are expressed in terms of partial pressures, which are then normalized using the total pressure. The initial composition of the gas ceiling is pure argon, avoiding the undesirable chemical disturbance of reactive gases such as O₂ or CO₂ on the radiolysis evolution.

2.4 Simulations

Simulations of radiolysis within the three mini-containers were performed with the CHEMSIMUL software (Kirkegaard et al. 2008). The latter manages simultaneously the production of primary water species, the secondary recombination reactions (about 60), the homogeneous acid-base equilibria, the heterogeneous solid-solution and solution-gas equilibria, the gas transport (diffusive and convective) in the porous material. The set of kinetic equations are numerically resolved for obtaining the quantities of all the species as a function of the irradiation time, in particular the quantity of H₂ in the gaseous roof of each mini-container (what is measured by the experiment). The calculations are performed for a variable temperature from the continuous record provided by the experiment. The activity correction of the ions in solution is based on the Debye-Hückel with the Davies extension model (the validity of which is ensured for I ≤ 0.3 mol kg⁻¹). For dosimetry, CHEMSIMUL considers the initial dose rate in pore water calculated by the Tripoly-4 code and updates it during radiolysis, taking into account the radioactive decay of the ⁶⁰Co source. It also calculates the integrated dose at each time. The objective of the simulations is both to know the contribution of the pore water alone to the H₂ production and to reproduce the experimental result by introducing an additional production term allowing to characterize the contribution of the solid phases.

3. Results

3.1 XRD characterization

The mineralogical composition of a hydrated calcium silicate paste irradiated for 6 months shows no change in comparison with the non-irradiated control material, both materials being examined at the same age of 16 months (Fig. 2). Both hydration products are detectable with the same intensities: portlandite with many well resolved diffraction lines and cementitious C-S-H with a very low crystallinity. The absence of residual anhydrous Ca₃SiO₅ allows to conclude that the hydration is complete. There is no trace of calcium peroxide octahydrate in the irradiated sample.

3.2 Gas measurements

The evolution of the total pressure is followed during 2, 4 and 6 months in the mini-containers respectively dedicated to each term, the gas analysis being carried out at the end of each corresponding irradiation time (Table 1 and Fig. 3).

After having checked by analysis of the gas phase that no other gas than H₂ is formed (O₂ in particular), we deduce that the increment of total pressure corresponds in this case to the increase of the partial pressure of H₂ (Fig. 3). Therefore, in Table 1, P(H₂) is obtained by assigning the H₂ percentage measured by mass spectrometry to the dry gas pressure [i.e., P_{total} - P(H₂O)].
on homographic functions \(\frac{at}{1 + bt}\).

The results obtained show that after 6 months, an equilibrium state is still not reached and that the behavior of the three samples shows a significant variability related to very close but not identical experimental conditions (mass of material and dose rate, see Table 2). Thus, the hierarchical order of the three kinetic curves appears approximately proportional to the product of the primary water production by the pore water mass. In this case, the individual kinetics of each mini-container appear much more relevant than the average evolution trying to pass through the four experimental points.

The pressure measured in the dead volume is not a complete information because dihydrogen is also present in the porosity of the material, both in gas phase and in pore solution. At each time, the porosity of the material is the seat of the primary production of \(\text{H}_2\) and of a local solubility equilibrium (Henry's law) corrected by the partial recombination of \(\text{H}_2\) with the oxidizing radicals of the radiolysis of water, the local pressure being modulated by the resistance to gas transport. Figure 4 illustrates this chemistry-transport coupling using an idealized cementitious material in a closed system. This representation corresponds to the situation usually modeled for which the contribution of solid phases to...
H$_2$ production is not taken into account. In this context where the steady state approximation can be invoked, the amount of H$_2$ available in the gas ceiling compared to the total amount in the system (gas ceiling + gas porosity + pore solution) defines the distribution fraction:

$$f_{H_2} = \frac{V_{\text{gas ceiling}}}{V_{\text{total system}}} = \frac{V_{\text{gas ceiling}}}{V_{\text{gas ceiling}} + V_{\text{gas porosity}} + V_{\text{liq porosity}}}$$

where $V$, $R$, $K_H$, and $[\text{H}_2\text{O}]+\sum[\text{solute}]$, indicate the volumes defining the system, ideal gas constant, Henry’s law constant for H$_2$ ($= 6.7745 \times 10^9$ Pa at $t_0$) and the sum of the molar concentrations of water and all solutes in pore liquid (≈ 55.965 mol dm$^{-3}$), respectively.

Close to 2/3 in the present case, the distribution fraction depends essentially on the respective gas and liquid volumes. Therefore, the primary production rate of the overall system (in mol s$^{-1}$) can be calculated from the volume of the gas ceiling and the value of the derivative of the adjustment function of $P(H_2)$ at $t = 0$ (Table 2):

$$\left(\frac{dH_2}{dt}\right)_{\text{system } t = 0} = \left(\frac{dH_2}{dt}\right)_{H_2} + \left(\frac{dH_2}{dt}\right)_{\text{system } t = 0} = \left(\frac{dP(H_2)}{dt}\right)_{H_2}$$

The average of the three samples gives:

$$\left(\frac{dH_2}{dt}\right)_{\text{system } t = 0} = (5.91 \pm 0.48) \times 10^{-10} \text{ mol} \cdot \text{s}^{-1}$$

Furthermore, the theoretical primary production rate of H$_2$ for free water is easily calculated from Eq. (4), where $m_{\text{res. w}}, G_{H_2 \text{w}}$ and $D'_{\text{H}_2\text{O}}$ represent the mass of residual pore water (kg) given by Eq. (8), primary yield (mol J$^{-1}$), and gamma dose rate in pore water (Gy s$^{-1}$), respectively:

$$\left(\frac{dH_2}{dt}\right)_{w} = m_{\text{res. w}} \times G_{H_2 \text{w}} (T, pH) \times D'_{\text{H}_2\text{O}}$$

At $t = 0$ where temperature and pH are respectively equal to 16.2°C and 13.53, the $G_{H_2 \text{w}}$ value is 4.10 $\times 10^{-8}$ mol J$^{-1}$ and the average of the three samples gives:

$$\left(\frac{dH_2}{dt}\right)_{w} = (1.03 \pm 0.04) \times 10^{-10} \text{ mol} \cdot \text{s}^{-1}$$

At this stage, the primary production rate of the system appears clearly higher than that due to bulk water alone, the contribution of which representing less than 20%. If we assume that the additional primary production is attributable to the apparent primary production of the solid phases (C–S–H and portlandite), it is then possible to deduce the apparent primary yield of the solid phases ($G_{H_2 \text{hydrates}}$) at time $t_0$:

$$P'(H_2) < P(H_2)$$

Gas transport:
- diffusion = $\Delta P(H_2)$
- convection = $\Delta P_{\text{total}}$

Transport resistance:
- saturation = $V_{\text{H}_2\text{O}}/V_{\text{porosity}}$

Henry’s law:
$P(H_2) = K_{H_2} \cdot x(H_2)$

Primary production:
$d[H_2]/dt = G(H_2) \cdot D' \cdot 10^{3} \cdot \rho_w$

H$_2$ recycling:
- $O^- + H_2 \rightarrow OH^- + H^+$
- $OH^- + H^+ \rightarrow O^- + H_2O$
- $e^- + HO_2^- \rightarrow O^- + OH^- + H_2O$

Fig. 4 Schematic representation of an idealized cementitious material in a closed system and highlights associated with each zone (contribution of solid phases, in grey, not taken into account).

| Sample | $m_{\text{paste}}$ (g) | $m_{\text{res. w}}$ (g) | $V_{\text{paste}}$ (cm$^3$) | $V_{\text{liq}}$ (cm$^3$) | $V_{\text{g. ceiling}}$ (cm$^3$) | $D'_{\text{H}_2\text{O}}$ (Gy s$^{-1}$) | $f_{H_2}$ | $(dP(H_2)/dt)_0$ (Pa s$^{-1}$) |
|--------|------------------------|-------------------------|-----------------|-----------------|-----------------|-----------------|----------------|------------------|
| “2 months” | 215.87 | 25.11 | 110.15 | 25.12 | 31.15 | 0.101 | 0.683 | 3.17 $\times 10^{-2}$ |
| “4 months” | 213.53 | 24.84 | 108.96 | 24.84 | 32.35 | 0.096 | 0.693 | 2.79 $\times 10^{-2}$ |
| “6 months” | 218.73 | 25.40 | 111.61 | 25.40 | 29.69 | 0.102 | 0.669 | 3.45 $\times 10^{-2}$ |
In this approach, it is necessary to know the mass of the hydrated products \( m_{\text{hydrates}} \) and the corresponding dose rate \( D'_{\text{hydrates}} \), which requires 1) to have an accurate balance of the hydration reaction of the initial tricalcium silicate, 2) to know the stoichiometry of the cementitious C-S-H and 3) to know the mass coefficients of energy absorption for the different phases (water and solid hydrates).

### 4. Discussion

#### 4.1 \( \text{Ca}_3\text{SiO}_5 \) hydration reaction

The stoichiometry of cementitious C-S-H can be determined by considering the hydration reaction of tricalcium silicate (Reaction R1) (Locher 1966), which results in the coexistence of two hydrates (C-S-H and portlandite):

\[
\text{Ca}_3\text{SiO}_5 + (3 - x + y) \text{H}_2\text{O} \rightarrow \text{Ca}_x\text{SiO}_{2y}(\text{H}_2\text{O})_{3x} + (3 - x) \text{Ca(OH)}_2 \quad (\text{R1})
\]

There is no consensus on the \( x \) and \( y \) coefficients because the quantity of water ensuring complete hydration depends on the initial state and on the heat treatment of the two hydrates obtained. Its measurement depends also on the technique used; therefore it varies significantly according to the authors. The term \( 3 - x + y \) is thus found to be equal to 2.66 (Locher 1966), 2.37 (Brouwers 2004) or even 3.10 (Allen et al. 2007). In the latter case, the determination was based on X-ray and neutron scattering experiments performed at small angles. An average value \( x = 1.7 \) is often cited for cementitious C-S-Hs in equilibrium with portlandite (Allen et al. 2007; Brouwers 2004; Lothenbach and Nonat 2015), but it includes C-S-Hs synthesized from \( \text{Ca(OH)}_2 \) and \( \text{SiO}_2 \). The value \( x = 1.8 \) most likely corresponds to the maximum value when C-S-H is formed upon hydration of \( \text{Ca}_3\text{SiO}_5 \) (Chen et al. 2004). This value was also used by (Allen et al. 2007). The study of the distribution of the different forms of water according to the "Defective Tobermorite-Like Model" (Roosz et al. 2016) for C-S-Hs having a Ca/Si ratio varying from 0.69 to 1.42 confirms this last hypothesis while specifying the partition of the different forms of bond water. Adjusting the experimental data for \( \text{HO}^-; \text{H}_2\text{O} \) and total \( \text{H}_2\text{O} = \frac{1}{2}\text{HO}^- + \text{H}_2\text{O} \) as a function of \( (\text{Ca/Si})^{2/3} \) (best fit) enables extrapolating a stoichiometric coefficient close to an integer value for each type of water when \( \text{Ca/Si} = x = \frac{11}{6} \approx 1.8 \) (Fig. 5), which is not the case with \( x = 1.7 \). As a result, considering the formation of cementitious C-S-H with 6 silicon atoms (typical for the tobermorite group) and the condition \( x = y \), the hydration reaction (Reaction R1) can be written as:

\[
6 \text{Ca}_3\text{SiO}_5 + 18 \text{H}_2\text{O} \rightarrow \text{Ca}_{11/6}\text{Si}_6\text{O}_{20}(\text{OH})_8 \cdot 8 \text{H}_2\text{O} + 7 \text{Ca(OH)}_2 \quad (\text{R2})
\]

The distribution of bound water types in the cementitious C-S-H is thus identical to that of jennite \( [\text{Ca}_{8/3}\text{Si}_6\text{O}_{18}(\text{OH})_8 \cdot 8 \text{H}_2\text{O}] \), characterized by a majority proportion of water of crystallization. By combining the molar mass of cementitious C-S-H with the density found by Allen et al. (2007), the resulting molar volume (Table 3) is close to that proposed by Allen et al. (2007) and by Jennings (2008), which indirectly validates the chosen stoichiometry. It should be noted that the interpretation of the values referring to the "fully hydrated"
C-S-H in Table 3 does not take into account the water adsorbed outside the particles.

4.2 Result of the hydration process

Application of the Powers-Brownyard model (Jensen and Hansen 2001) provides the amounts of hydrates formed, the amount of bound water, and the amount of residual water based on the complete hydration of the tricalcium silicate (Reaction R2), knowing the mass of the latter in the samples. From the molar weights recalled in Table 3, the mass proportion of bound water (non-evaporable water) required for the constitution of cementitious C-S-H and portlandite together is given by:

\[
\left(\frac{w}{c}\right)_n = \frac{18 \times M_{H_2O}}{6 \times M_{Ca_3SiO_5}} = 0.2367
\]

For a given mass of tricalcium silicate and w/c ratio, the residual pore water mass and bound water mass after complete hydration (progress rate \(\alpha = 1\)) are respectively:

\[
m_{\text{res. w}} = m_{c,5} \times \left(\frac{w}{c}\right)_n \\
m_{\text{bound w}} = m_{c,5} \times \alpha \left(\frac{w}{c}\right)_n
\]

Moreover, the mass of hydrates obtained for a given mass of tricalcium silicate is deduced from the Reaction R2:

\[
m_{\text{hydrates}} = m_{c,5} \times \frac{7 \times M_{\text{pore}} + M_{C-S-H}}{6 \times M_{Ca_3SiO_5}} = m_{c,5} \times \left(1 + \left(\frac{w}{c}\right)_n\right)
\]

\[
= m_{c,5} \times 1.2367
\]

4.3 Dose rate in solid hydrates

The dose rate in hydrates (portlandite and cementitious C-S-H together) can be calculated as a first approximation from the dose rate in water by considering proportionality with the respective energy absorption mass coefficients [Eq. (11)]. For the average energy of the two \(^{60}\text{Co}\) \(\gamma\) emissions (\(E = 1253\) keV), the coefficients calculated from the elemental chemical composition (Hubbell and Seltzer 2004) are equal to \((\mu_m/\rho)_{H_2O} = 0.02963\) cm\(^2\)/g and \((\mu_m/\rho)_{\text{hydrates}} = 0.02685\) cm\(^2\)/g, respectively. The dose rate correction with respect to water then gives:

\[
D'_{\text{hydrates}} = D'_{H_2O} \left(\frac{\mu_m}{\rho}_{\text{hydrates}}\right) = D'_{H_2O} \times 0.9062
\]

4.4 \(H_2\) primary yield of hydrates

Equation (6) is used to determine a primary yield of \(H_2\) production for the two undifferentiated cementitious hydrates in the three samples (Table 4). The \(H_2\) primary yield of hydrates (average obtained for the three samples) is \((G_{H_2})_{\text{hydrates}} = (2.84 \pm 0.13) \times 10^8\) mol J\(^{-1}\) and is found to be of the same order of magnitude as the value determined by LaVerne for portlandite alone (2.07 \times 10^8 mol J\(^{-1}\)).

In light of the previous results, cementitious hydrates appear to contribute to primary \(H_2\) production. For the overall simulation of the radiolysis of the cementitious material, the primary source term can therefore be considered as resulting:

- From the decomposition of the pore solution, assimilated to that of the solvent (diluted solution in the sense of the ionic strength), generating all the

| Sample        | \(\frac{dH}{dt}\)\_system\_\(t=0\) (mol s\(^{-1}\)) | \(\frac{dH}{dt}\)\_hydrates\(t=0\) (mol s\(^{-1}\)) | \(m_{\text{hydrates}}\) (kg) | \(D'_{\text{hydrates}}\) Gy s\(^{-1}\) | \((G_{H_2})_{\text{hydrates}}\) (mol J\(^{-1}\)) |
|---------------|-----------------------------------------------|-----------------------------------------------|-----------------------------|------------------------------------------|-----------------------------------------------|
| "2 months"   | \(5.998 \times 10^{-10}\)                      | \(1.038 \times 10^{-10}\)                     | \(4.960 \times 10^{-10}\)  | \(0.1902\)                               | \(0.0915\)                                    |
| "4 months"   | \(5.394 \times 10^{-10}\)                      | \(9.758 \times 10^{-11}\)                     | \(4.419 \times 10^{-10}\)  | \(0.1881\)                               | \(0.0870\)                                    |
| "6 months"   | \(6.346 \times 10^{-10}\)                      | \(1.062 \times 10^{-10}\)                     | \(5.284 \times 10^{-10}\)  | \(0.1927\)                               | \(0.0924\)                                    |
primary species (H₂, H₂O₂, and radicals H*, e_\text{aq}^-, \text{HO}^•),

2) From the rupture of O–H bonds constituting the crystal lattice of the hydrates, leading to the formation of H₂, without prejudging a particular mechanism.

It is important not to confuse this last mechanism with the transfer of energy from the solid to the surface water leading to radiolysis already taken into account when considering "free" (unbound) water. On this point it should be noted that in the calculation of the energy deposition in water (averaged over the material), the "energy transfer" component is implicitly taken into account when the KERMA rate is used as a substitute for the absorbed γ dose rate.

In order to recover the experimental evolution of P(H₂) over a period of 6 months, the simulation of the radiolysis of a fully hydrated tricalcium silicate paste is now possible using the additional source term determined above for the corresponding sample (Table 4).

In this approach, three different simulation options can be tested and compared (Fig. 6) with respect to the experimental data. 1) Considering only the radiolysis of pore water alone, the simulated partial pressure of H₂ computed in the gas ceiling of the mini-container is significantly lower than in the experiment. 2) By adding the specific source term for solid hydrates, the simulated curve ("pore water + hydrates 1" curve) coincides well with the experimental evolution in its initial part but leads to much higher pressures in the end. This is because the additional production of H₂ by hydrates is not compensated by the production of oxidizing radicals that can destroy it in pore solution. 3) A constant primary yield for solid hydrates not being compatible with the experimental results, it must be admitted that it is necessarily decreasing with time or dose. If we consider that the formation of H₂ within solid hydrates proceeds from the breaking of O–H bonds and that the phenomena of diffusion and recombination are much more constrained in a solid phase than in a liquid phase, it is possible to envisage a decrease in the number of bonds statistically eligible for breaking with time. In this hypothesis, an exponential decrease, characteristic of a mechanism occurring with equal probability in time, but not associated with an aging phenomenon is a possible description. Indeed, the application of an exponentially decreasing primary yield [Eq. (12)] for only the cementitious hydrates allows to recover the shape of the experimental curve ("pore water + hydrates 2" curve).

$$\left(G_{H_2}\right)_{\text{eff, hydrates}} = \left(G_{H_2}\right)_{\text{hydrates}} \times e^{-5.9 \times 10^{-7} t}$$  \hspace{1cm} (12)

Without referring to a particular “saturation” mechanism, the effective H₂ yield for hydrates, expressed as a function of the dose deposited in them (D_{hydrates}), shows that the extinction of this additional H₂ source term reaches 99% shortly after 1 MGy in the case of the "6 months" sample (Fig. 7).

For the other samples, the characteristics are similar (Table 5) although slightly different, probably due to an adjustment on shorter durations less affected by temperature variations. Overall, the average dose characterizing the decay process is about 200 kGy. The integrated

| Sample       | \(\left(G_{H_2}\right)_{\text{hydrates}}\) (mol J⁻¹) | Characteristic dose (MGy) |
|--------------|-----------------------------------------------|----------------------------|
| "2 months"  | \(2.85 \times 10^{-8} \times e^{-5.82 D_{hydrates}}\) | 0.172                      |
| "4 months"  | \(2.70 \times 10^{-8} \times e^{-5.78 D_{hydrates}}\) | 0.173                      |
| "6 months"  | \(2.97 \times 10^{-8} \times e^{-4.25 D_{hydrates}}\) | 0.235                      |

Fig. 6 H₂ pressure in the gas ceiling during the γ radiolysis of Ca₃SiO₅ paste: fitted experimental data (red curve) and simulations (blue curves).
dose $D_{\text{hydrates}}$ calculated by CHEMSIMUL takes into account the radioactive decay and the correction in the solid phases [Eq. (11)].

Several remarks can be made about this behavior. If the contribution of hydrates to $H_2$ formation is dose-dependent, experiments conducted with different protocols logically lead to different yields, which may explain the dispersion of the published values (Acher 2017; LaVerne and Tandon 2005; Yin et al. 2019). Concerning the origin of the extinction of $H_2$ production by hydrates, it is not possible at this stage to know which hydrate produces the most $H_2$ and what the mechanism is. The decreasing primary production suggests, among different hypotheses, a saturation phenomenon linked either to a more and more limited number of $O\cdot H$ bonds accessible to rupture, or to a recombination of $H_2$ precursors, if not of $H_2$ itself, by a process still to be determined, possibly thermo-activated. At this time, an upper limit on the initial effective primary yield of each solid hydrate (at $t_0$) can be estimated by considering the stoichiometry of the $R2$ reaction. Assuming that the dose rate is almost identical for each hydrate, the relationship between the different effective initial yields is given by Eq. (13):

$$
\left(3M_{\text{CaSiO}} + 7M_{\text{Ca(OH)}}\right) \cdot G(H_2)_{\text{hydrates}} = 3M_{\text{CaSiO}} \cdot G(H_2)_{\text{C-S-H}} + 7M_{\text{Ca(OH)}} \cdot G(H_2)_{\text{Ca(OH)}}
$$

From the molar masses (Table 3) and the experimental average $G(H_2)_{\text{hydrates}} = 2.84 \times 10^{-8}$ mol/J, we obtain $G(H_2) < 4.1 \times 10^{-8}$ mol/J for C-S-H and $G(H_2) < 9.3 \times 10^{-8}$ mol/J for portlandite. If the effective primary yield of portlandite alone is determined elsewhere, the value corresponding to the cementitious C-S-H can be deduced immediately (Fig. 8).

Concerning the global behavior of the system (cementitious material with pore water and gaseous porosity), the simulations show that the initial contribution of an additional quantity of $H_2$ (to that resulting from the radiolysis of water) stresses the recycling chain reaction equivalent to the «Allen chain» (Allen 1948) in alkaline medium (Reactions R3 to R5).

$$
\begin{align*}
O^- + H_2 &\rightarrow OH^- + H^+; \\
&k = 1.3 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ at } 25^\circ C \\
\text{OH}^- + H^+ &\rightarrow e^- + H_2O; \\
&k = 2.4 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ at } 25^\circ C \\
e^- + \text{HO}_2 &\rightarrow \text{O}^2 + \text{OH}^- + \text{H}_2\text{O}; \\
&k = 3.5 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \text{ at } 25^\circ C
\end{align*}
$$

The additional source term disappears with time, resulting in a strong transient anomaly in the evolution of the $H_2$ recycling rate before gradually reaching the maximum value around 6 months (Fig. 9). At this time, it can be assumed that radiolysis is completely regulated within the system and that the rate of $H_2$ destruction is equal to the rate of primary production.

With a dual primary production (pore water + solid hydrates), the recycling rate is calculated according to Eq. (14) where the actual $H_2$ production rate is the resulting combination of the total primary production rate with the kinetics of all secondary reactions in pore water (all rates expressed in mol dm$^{-3}$/s):

$$
R = 1 - \frac{\left(\frac{d}{dt}\sum[H_2]\right)_{\text{actual}}}{\left(\frac{d[H_2]}{dt}\right)_{\text{primary w}} + \left(\frac{d[H_2]}{dt}\right)_{\text{primary hydr.}}}
$$

![Fig. 7 Effective $H_2$ primary yield specific to Ca$_3$SiO$_3$ hydration products as a function of the gamma dose in the hydrates (from experiment "6 months").](image-url)
In Eq. (14), \[ \frac{d[H_2]}{dt} \] \_primary-w and \[ \frac{d[H_2]}{dt} \] \_primary-hyd. are the primary production from pore water (= constant) and primary production from solid hydrates (with decreasing \( G(H_2)_{hydrates} \) defined in Table 5), respectively. Peak recycling occurs relatively early (between 5 and 7 days depending on the sample). It is accompanied by a deep change in the chemical evolution of the pore environment that will continue thereafter. This change consists of a drastic drop in \( O_2 \) concentration and a switch to a frankly reducing regime. The phenomenon is well illustrated by the evolution of the redox potential of the pore solution (Fig. 10) calculated on the basis of the fast couple \( O_2^{aq}/O_2^{•−} \) \[ (E_{O_2 aq/O_2}^{eq}) = −0.18 \text{ V vs NHE (Koppenol et al. 2010)}) \]

\[ E_{O_2 aq/O_2}^{eq} = E^{0}_{O_2 aq/O_2} + \frac{R T}{n F} \ln \left( \frac{[O_2^{aq}]}{[O_2^{−}]} \right) \]

The redox potential reached at equilibrium (~470 mV) corresponds to an extremely low concentration of \( O_2 \) in pore solution, of the order of \( 10^{-19} \text{ mol dm}^{-3} \). As this phenomenon is consecutive to the \( H_2 \) recycling peak,
it is concluded that the disappearance of O$_2$ in most of the irradiated cementitious matrices could originate from the effect of the additional H$_2$ source term due to the hydrated solid phases and not from the possible conversion into calcium peroxide octahydrate (Bouniol and Aspart 1998). Concomitant with the fall of the redox potential, the fall of the peroxide concentration (H$_2$O$_2$ + HO$_2^-$ + O$_2^{2-}$) highlighted by simulation shows that it is strongly consumed (Reaction R5) and that it cannot therefore accumulate. For comparison, the potential calculated without taking into account the radiolytic behavior of hydrates has a much higher value (Fig. 10). The slight increase from $-174$ to $-135$ mV corresponds in this case to O$_2$ concentrations between $1.3 \times 10^{-5}$ and $1.85 \times 10^{-4}$ mol dm$^{-3}$.

Beyond the particular and transient phenomenon highlighted with the radiolysis of hydrated cementitious phases, the impact of an additional source of H$_2$ on the radiolytic evolution of the whole system (solid phases + pore water) is probably always the same. It leads to a regulation of radiolysis and to the achievement of an equilibrium, provided that the system is closed or sufficiently confined (limited H$_2$ leakage) to keep the efficiency of the recycling chain reaction (R3-R5). Any configuration where dihydrogen is produced in addition to the water radiolysis is potentially affected by this mechanism, for example sulfide-rich cementitious matrices (additional production by the H$^+$ + H$_2$S reaction (Bouniol et al. 2018)) or cementitious matrices hosting an internal (anoxic) metal corrosion process.

5. Conclusion

An initial global contribution of the hydrated solid phases to the radiolytic production of H$_2$ (the respective contributions of the cementitious portlandite and C-S-H are not explained) was highlighted by a systemic approach of the gamma irradiation of a tricalcium silicate paste. In this approach, the balance of the tricalcium silicate hydration reaction takes an essential part in the definition of the system. This balance sheet uses the following stoichiometry: $6 \text{Ca}_3\text{SiO}_5 + 18 \text{H}_2\text{O} \rightarrow \text{Ca}_{11}\text{Si}_6\text{O}_{20}(\text{OH})_6 8 \text{H}_2\text{O} + 7 \text{Ca(OH)}_2$. The attempt to reproduce experimental results by simulation suggests that pore water and solid hydration products are non-analogous primary sources of H$_2$: H$_2$ and full set of primary species for water (including HO$^*$ radicals for recombination), H$_2$ alone for solid hydrates. Consequently, the effect of an additional source of H$_2$ in a closed system results in a very efficient regulation of radiolysis via recycling in the pore solution (Allen chain in basic medium). The coupling of the two primary productions with the secondary reactions of water radiolysis shows that if there is a contribution of solid hydrates (initial experimental production), it must be necessarily decreasing in order to be consistent with the experimental production at term. The initial primary yield of H$_2$ attributable to the hydrated solid phases is on the order of $2.8 \times 10^{-8}$ mol J$^{-1}$, a value about 30% lower than the G(H$_2$) of water. The average dose characterizing the decay process is about 200 kGy. Therefore, the short-term behavior is not representative of the long-term evolution and a radiolytic H$_2$ production extrapolated from too short experiments may lead to an overestimation. In the context of long-term irradiation (concretes for radiation shielding, cement matrices for radwastes), the impact of the non-permanent radiolytic contribution of solid hydrates could be negligible compared to that of pore water.

![Fig. 10 Redox potential of the pore solution simulated with the O$_{2aq}$/O$_{2^-}$ couple, considering the water radiolysis alone or the additional decreasing source-term H$_2$ in Ca$_3$SiO$_5$ paste irradiated for 6 months (simulation).](image-url)
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