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Radioactive waste conditioning: the choice of the cement matrix versus irradiation

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ABSTRACT

The aim of this study is to compare the behavior of Portland and Ciment Fondu® cement under irradiation taking into account both real cement pastes and synthetic hydrates. First, γ -irradiations were performed using a ^{60}Co source (dose rate: 0.17 - 0.25 Gy.s⁻¹, dose: up to 500×10^3 Gy). Thermogravimetric analysis measurements were performed in order to determine the amount and the type of water involved. H_2 gas production was measured by gas chromatography. Regardless of the water to cement ratio (W/C) chosen (0.2, 0.4 and 0.6), it is shown that Ciment Fondu® pastes produce less H_2 under irradiation. Moreover, the H_2 production of portlandite and gibbsite, constituent hydrates of Portland and Ciment Fondu® cements respectively, shows that the amount of gas produced depends on the hydrate nature. Secondly, portlandite and gibbsite were electron-irradiated up to 300 MGy and 3 GGy using the LSI SIRIUS accelerator platform. X-Ray Diffraction analyses were performed before and after irradiation in order to investigate structural damage. Only limited structural disorder was observed, which confirms the good stability of both hydrates under present irradiation conditions.

1. INTRODUCTION

Nowadays, Portland cement based matrices are widely used for conditioning and embedding nuclear waste. The literature reports a large number of studies on the impact of radiations on this type of material in order to demonstrate the validity and the sustainability of this solution [1, 2, 3]. The interaction between the ionizing radiation and the matrix leads to (i) radiolysis gas production, mainly H_2 , which has to be minimized (ii) mechanical, textural and mineralogical modifications.

Furthermore, due to the multiplicity and the complexity of the types of nuclear waste to be treated, alternative matrices to Portland cement are required.

Recent unpublished results show a factor of three in the H_2 radiolytic yield between Portland and Fondu® cement. Our aim is to compare the behavior of these two cements under irradiation taking into account both real cement pastes and synthetic hydrates. Two aspects are considered: H_2 production and structural

damage. In first approximation, two hydrates are considered: portlandite $\text{Ca}(\text{OH})_2$, one of the main constituent of Portland cement and gibbsite $\text{Al}(\text{OH})_3$, one of the main constituent of Ciment Fondu® cement (part of the Calcium Aluminate Cements (CAC)).

Throughout the paper, in order to simplify the chemical formula of the various compounds discussed below, we use the shorter oxide abbreviations: C = CaO , S = SiO_2 , A = Al_2O_3 , F = Fe_2O_3 , T = TiO_2 , H = H_2O .

2. EXPERIMENTAL

Sample Preparation and Characterization

Portland (60 % C_3S , 20 % C_2S , 19 % C_4AF and 1 % others) and Ciment Fondu® (50 % CA, 8 % C_4AF , 8 % $\beta\text{-C}_2\text{S}$, 8 % C_3FT , 7 % Fe_3O_4 and 19 % others) cements were used. Cements were mixed with distilled water with a W/C ratio equal to 0.2, 0.4 and 0.6. Samples will be referred to as Portland-0.2, Fondu-0.2 and so on increasing the number according to the W/C ratio. Portland paste maturation occurred in sealed tubes, at room temperature, in order to

limit atmospheric exchanges. Ciment Fondu® samples were cured at room temperature under 98 % of relative humidity during one week and then heated at 50 °C during one more week in order to ensure the total conversion of the metastable hydrates. Thermal Gravimetric Analysis (TGA, Netzsch STA 409 instrument, heating rate: 10 K.min⁻¹ under nitrogen atmosphere, from room temperature to 1000 °C) were performed in order to determine the amount and type of water.

Portlandite CH (VWR Chemicals Prolabo®, 96 %) and gibbsite AH₃ (Merck, 99,6 %) commercial samples were used. For gas measurements, these hydrates had the advantage of only containing hydroxyl groups, consequently a heat treatment up to 150 °C during 48 hours in order to eliminate adsorbed water is possible. The amount of water was checked by TGA; a plateau is observed for both hydrates up to 200 °C. X-Ray Diffraction analysis were performed before and after electron irradiation in order to investigate any possible structural damage. Powder XRD analysis were performed using a PANalytical diffractometer, with a fast detector (X-celerator), in the Bragg Brentano geometry (CuK_α radiation, $\lambda_{K\alpha1} = 1.540596 \text{ \AA}$ and $\lambda_{K\alpha2} = 1.544410 \text{ \AA}$). All the data were collected in the same conditions, in the angular range $5^\circ < 2\theta < 90^\circ$, with step intervals of 0.02° (2θ) and scan set time of 1.5 hours. Rietveld refinements were performed using the TOPAS software (version 4, Bruker-AXS, Karlsruhe, Germany, 1996–2007) based on the fundamental parameters approach [4].

Irradiation Experiments

Two types of irradiation experiments were performed:

(i) gamma irradiation at low doses: Irradiations were conducted using a ⁶⁰Co source of the Gammatec facility (Steris, France). Cement pastes, CH and AH₃ were irradiated up to 600 kGy at 900 Gy/h and up to 200 kGy at 600 Gy/h respectively in order to determine their hydrogen radiolytic yield.

(ii) electron irradiation at “high” doses: Small pellets (13 mm diameter and 1 mm thickness) of CH and AH₃ were irradiated using the LSI SIRIUS accelerator platform. Electrons of 2.5 MeV were used. At this energy, all electrons pass through the sample (projected range was 4 mm). Irradiation conditions are summarized in table 1. Adsorbed doses were estimated using ESTAR code [5].

Table 1. Electron irradiation conditions

	CH		AH ₃	
Current (μA)	20	25	29	24
Flux ($\times 10^{13} \text{ e}^- \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$)	7.0	8.8	10	8.5
Dose (MGy)	300	3 000	230	2500
Temperature (°C)	<43	<49	41	41

H₂ Determination

Hydrogen production was measured by gas chromatography (Varian CP-3800 instrument equipped with a thermal conductivity detector and a molecular sieve-type column, furnace and detector temperature: 35 °C and 120 °C respectively). Argon was used as carrier gas. About 10 mL of gas were manually injected for each measurement. The radiolytic yield in H₂, G(H₂), is given by the slope of the linear regression of the number of moles of hydrogen (per kilogram of material), plotted versus the dose.

3. RESULTS

Low doses gamma irradiation

Portland and Ciment Fondu® pastes

The hydrogen production of Ciment Fondu® pastes irradiated under γ-rays was measured. The impact of the type of matrix and the water content (related to the W/C ratio) on the hydrogen production are both explored.

The radiolytic yields in H₂, G(H₂) as a function of the W/C ratio is sketched in Figure 1. It appears that H₂ production depends on the type of cement. Up to W/C = 0.4, Fondu® cement pastes produce three times less than Portland cement. At W/C = 0.6, the gap between the G(H₂) values is not significant ; the type of matrix seems to not matter anymore.

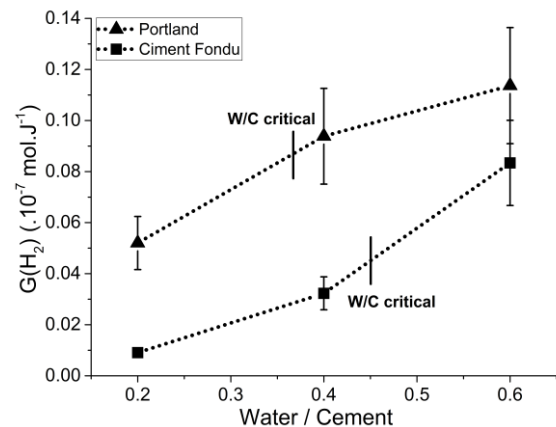


Figure 1. Portland and Ciment Fondu® radiolytic yield versus the water to cement ratio

These observations are consistent with TGA results (Figure 2).

At W/C equal to 0.2, Ciment Fondu® paste only contains adsorbed water whereas Portland cement contains free water, in particular due to the presence of Calcium Silicate Hydrates (C-S-H). Note that the presence of adsorbed water was confirmed by washing Fondu-0.6 sample with isopropanol and heating it up to 60 °C in order to eliminate residual water. The TGA curve obtained is the same as the one obtained for Fondu-0.2 sample.

At W/C equal to 0.6, the amount of free water is important in both matrices, which should explain the lower gap between $G(H_2)$ values.

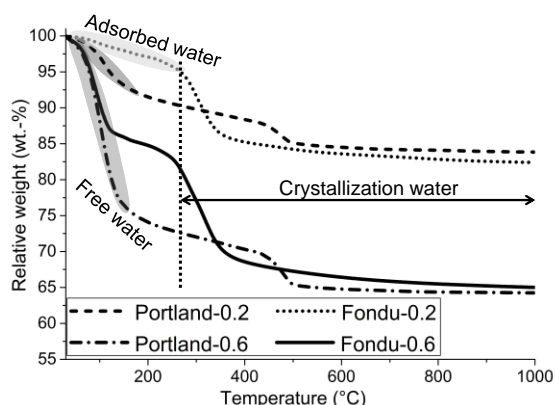


Figure 2. Portland and Ciment Fondu® pastes water content. TGA shows three types of water: 1) adsorbed water below 250 °C in Fondu-0.2, 2) free water below 250 °C in Portland-0.2, Portland-0.6 and Fondu-0.6, 3) crystallization water for all samples above 250 °C.

Portlandite CH and gibbsite AH_3 samples

The hydrogen production of portlandite CH and gibbsite AH_3 samples irradiated under γ -rays and heated up to 150 °C was measured. Their water content was measured by TGA (Figure 3). No adsorbed water is detected in both hydrates. CH and AH_3 contains respectively 21.8 % and 29 % water as hydroxyls groups.

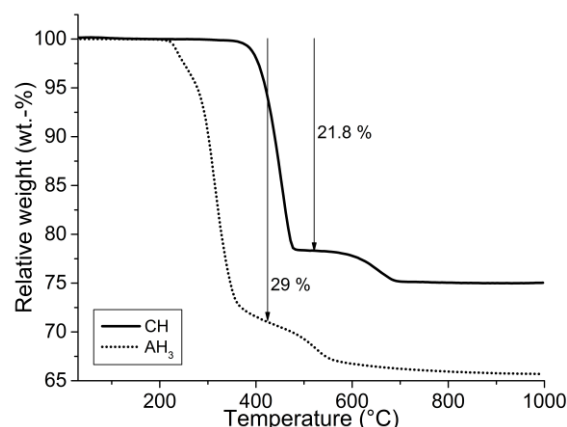


Figure 3. Portlandite (CH) and gibbsite (AH_3) water content (after heat treatment up to 150 °C during 48 hours). TGA shows an absence of adsorbed water for both hydrates.

The radiolytic yields in H_2 measured on both hydrates are the following:

$$G(H_2)(CH) = (0.042 \pm 0.004) 10^{-7} \text{ mol.J}^{-1};$$

$$G(H_2)(AH_3) = (0.009 \pm 0.005) 10^{-7} \text{ mol.J}^{-1};$$

When normalized to the total amount of water contained in CH and AH_3 , 21.8 % and 32.9 % respectively, radiolytic yields are equal to 0.19 mol.J^{-1} and $0.027 10^{-7} \text{ mol.J}^{-1}$. In comparison, the primary yield of bulk water is equal to $0.45 10^{-7} \text{ mol.J}^{-1}$. So, it appears that (i) both hydrates produce hydrogen under irradiation, and (ii) this production is different between CH and AH_3 whereas the same type of water is engaged.

Concluding remark

The radiolytic yield results obtained on cement pastes and synthetic hydrates are consistent. Both Portland cement paste and CH produce more hydrogen under gamma irradiation than Ciment Fondu® paste and AH_3 respectively. For future studies, it appears that the study of the hydrates should really help us to improve the understanding of the H_2 production of cement matrices.

High doses electron irradiation

Portlandite CH and gibbsite AH_3 structural resistance under electron irradiation was investigated by XRD. Not irradiated, irradiated up to 270 (310) MGy and up to 3.5 (3.0) GGy CH (AH_3) results are shown in Figure 4 and Figure 5.

Powder XRD patterns give intensity, width, position and also shape of each individual Bragg peaks, which can be associated to a structural arrangement of the material under study.

The main results of Figure 4 and 5 are the following:

In portlandite, (i) the intensity decreases following electron irradiation; (ii) there is an asymmetric broadening of some Bragg lines and (iii) an anisotropic shift of the Bragg lines positions.

In gibbsite, similar effects are observed, but less pronounced. However, due to the more complex atomic structure of gibbsite (monoclinic) compared to portlandite (rhombohedral), the interpretation of the results is made more difficult.

Finally experimental results clearly show that Portlandite and gibbsite are both resistant to electron irradiation at high doses (no amorphization, not even a beginning of amorphization). As for portlandite a slight

increase of interlayer spacing is seen with no consequence on the overall structural integrity. Work is in progress (using Electron Paramagnetic Resonance spectroscopy) in order to estimate the proper role of electron irradiation on the hydrogen bonding in these compounds.

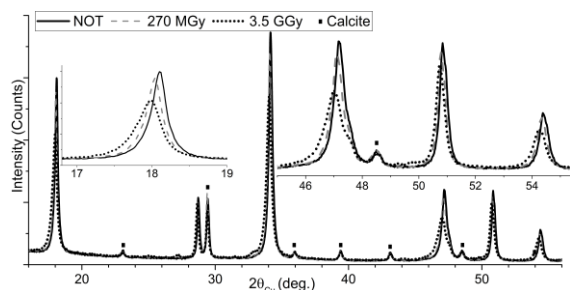


Figure 4. X-Ray diffraction pattern of portlandite Ca(OH)_2 : before irradiation and after electron irradiation at two doses (270 MGy, 3.5 GGy).

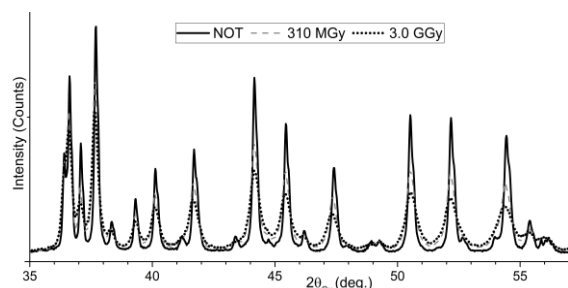


Figure 5. X-Ray diffraction pattern of gibbsite Al(OH)_3 : before irradiation and after electron irradiation at two doses (310 MGy, 3 GGy).

3. CONCLUSIONS

This study on Portland and Fondu® cements highlights (i) a significant dependence of the composition of the hydrates on the H_2 production and (ii) a rather low impact of electron radiations on the structure. A complementary study on other hydrates is currently underway.

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