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► To cite this version:

Loren Acher, Adeline Dannoux-Papin, Jérémy Haas, Mireille Courtial, Marie-Noëlle de Noirfontaine, et al.. Influence of the cement composition on the radiolytic behavior under irradiation. NUWCEM 2018 - Cement-based materials for nuclear wastes, Oct 2018, Avignon, France. hal-02312030

HAL Id: hal-02312030

<https://hal.science/hal-02312030>

Submitted on 9 Jul 2021

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Influence of the cement composition on the radiolytic behavior under irradiation

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Keywords: irradiation, aluminous cement, radiolysis, Portland cement

Abstract

Cement based materials are used for the conditioning of Low and Intermediate Level Wastes (LILW) due to their low cost, their ease of making and their ability to immobilize radioelements. Nevertheless, hydrogen gas is produced radiolytically under irradiation. For the safety of nuclear waste disposals, it is important to limit as much as possible the hydrogen gas release.

A comparison of the behavior of Portland and Ciment Fondu® cements under irradiation taking into account both real cement pastes and synthetic hydrates was performed to find out the role of the cement composition on the radiolytic behavior under irradiation. First, γ -irradiations were performed using a ⁶⁰Co source (dose rate: 0.17 - 0.25 Gy.s⁻¹, dose: up to 500×10³ Gy). Thermogravimetric analysis measurements were performed in order to determine the amount and the type of water involved. H₂ 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 H₂ under irradiation. In agreement with a recent study by Kadissy *et al.* [1], it is shown that the amount of gas produced by portlandite and gibbsite, which are respectively the constitutive hydrates of Portland and Ciment Fondu® cements, strongly depends on the nature of the hydrate. Secondly, portlandite and gibbsite were irradiated by electrons up to 270 MGy and 3.5 GGy using the LSI SIRIUS accelerator platform. X-Ray Diffraction analyses were performed before and after irradiation in order to investigate the structural damage. Despite some observed disorder, results show a good structural stability for both hydrates under irradiation.

1. Introduction

Portland cement is the most common material used for conditioning and embedding of nuclear wastes. 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 [2, 3, 4]. The interaction between the ionizing radiation and the matrix leads to (i) radiolysis gas production, mainly H₂, which has to be minimized, in order to avoid explosion risk (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 to optimize the costs of the waste conditioning.

As a result of a recent experimental work, it appears that there is a strong difference in the H₂ radiolytic yield between Portland and Fondu® cement which deserve to be more deeply investigated. In this paper, we compare the behavior of these two cements under irradiation taking into account both real cement pastes and synthetic hydrates. Two aspects are considered: H₂ production and structural damage. As a first approximation, two hydrates are considered: portlandite Ca(OH)₂, one of the main constituent of Portland cement and gibbsite Al(OH)₃, one of the main constituent of Ciment Fondu® cement (part of the Calcium Aluminate Cements (CAC)).

In order to simplify the chemical formula of the various compounds discussed below, the shorter oxide abbreviations are used: C = CaO, S = SiO₂, A = Al₂O₃, F = Fe₂O₃, T = TiO₂, H = H₂O.

2. EXPERIMENTAL

2.1. Sample Preparation and Characterization

Portland cement (60 % C₃S, 20 % C₂S, 19 % C₄AF and 1 % others) and Ciment Fondu® cement (50 % CA, 8 % C₄AF, 8 % β-C₂S, 8 % C₃FT, 7 % Fe₃O₄ and 19 % others) 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 % purity) and gibbsite AH₃ (Merck, 99,6 % purity) 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 (so – called dry samples). The amount of water was checked by TGA; a plateau is observed for both hydrates up to 200 °C. X-Ray Diffraction analysis was 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, λ_{Kα1} = 1.540596 Å and λ_{Kα2} = 1.544410 Å). All the data were collected in the same conditions, in the angular range 5° < 2θ < 90°, 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 [5].

2.2 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 [6].

Table 1. Electron irradiation conditions

	CH		AH ₃	
Current (μA)	20	25	29	24
Flux (×10 ¹³ e ⁻ .cm ⁻² .s ⁻¹)	9.5	9.6	10	8.5
Dose (MGy)	270	3 500	230	2500
Temperature (°C)	<43	<49	41	41

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

3.1. Low doses gamma irradiation

3.1.1. 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 H_2 , $G(H_2)$ as a function of the W/C ratio is sketched in Figure 1. It appears that H_2 production depends on the type of cement. Up to $W/C = 0.4$, Fondu® cement pastes produce three to five times less H_2 than Portland cement. At $W/C = 0.6$, the gap between the $G(H_2)$ values is insignificant ; the type of matrix seems not to matter anymore.

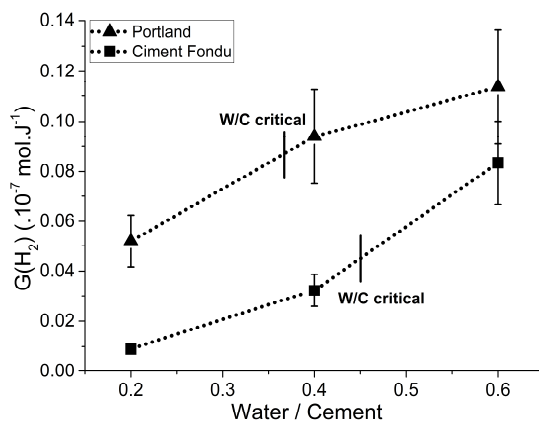


Figure 1. Portland and Ciment Fondu® radiolytic yield versus the water to cement ratio

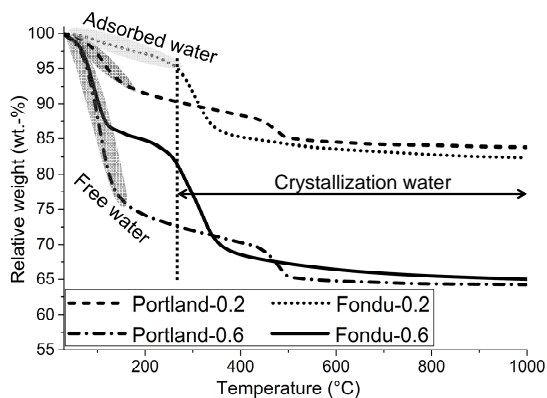


Figure 2. Portland and Ciment Fondu® pastes water content. TGA shows three types of water: 1) adsorbed water below 250 °C in Fondu-0.2, 2) free water below 250 °C in Portland-0.2, Portland-0.6 and Fondu-0.6, 3) crystallization water for all samples above 250 °C.

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. We can also note that in spite of the absence of free water, i.e. w/c ratio lower than w/c critical, cementitious materials still produce radiolytic gas. This shows that the water content of the hydrate (referred to as structural water, chemically bound water or crystallization water) has to be considered, in agreement with Kadissy *et al.* [1].

At W/C equal to 0.6, above w/c critical, the amount of free water is important in both matrices, which should explain the lower gap between $G(H_2)$ values: in this case the radiolytic yield is mainly attributed to free water.

3.1.2. Portlandite (CH) and gibbsite (AH₃) samples

The hydrogen production of portlandite CH and gibbsite AH₃ 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 AH₃ contains respectively 21.8 % and 29 % water as hydroxyl groups.

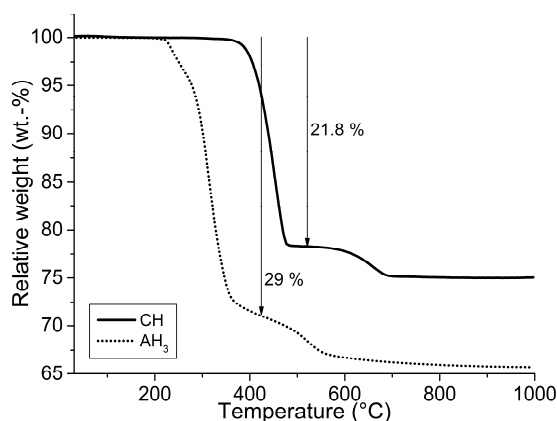


Figure 3. Portlandite (CH) and gibbsite (AH₃) water content (after heat treatment up to 150 °C during 48 hours). TGA shows an absence of adsorbed water for both hydrates.

The radiolytic yields in H₂ measured on both hydrates are the following:

$$G(\text{H}_2)(\text{CH}) = (0.042 \pm 0.004) 10^{-7} \text{ mol.J}^{-1};$$

$$G(\text{H}_2)(\text{AH}_3) = (0.009 \pm 0.005) 10^{-7} \text{ mol.J}^{-1};$$

When normalized to the total amount of water contained in CH and AH₃, 21.8 % and 32.9 % respectively, the radiolytic yields are equal to 0.19 mol.J⁻¹ and 0.027 10⁻⁷ mol.J⁻¹. In comparison, the primary yield of bulk water is equal to 0.45 10⁻⁷ mol.J⁻¹. We observe that (i) both hydrates produce hydrogen under irradiation, but (ii) that the H₂ yield differs between CH and AH₃.

3.1.3. 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 AH₃ respectively. For future studies, it appears that the study of the hydrates should really help to improve the understanding of the H₂ production of cement matrices.

3.2. High doses electron irradiation

Portlandite CH and gibbsite AH₃ 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 (AH₃) 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, i.e. no amorphization. As for portlandite a slight increase of the interlayer spacing is seen with no consequence on the overall structural integrity.

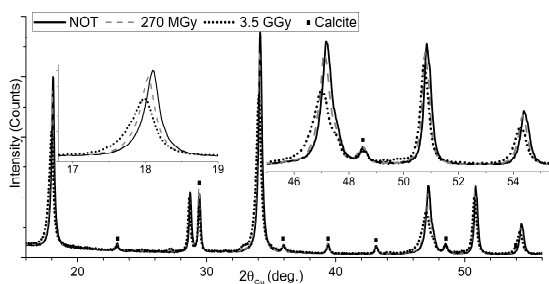


Figure 4. X-Ray diffraction pattern of portlandite Ca(OH)₂: before irradiation and after electron irradiation at two doses (270 MGy, 3.5 GGy).

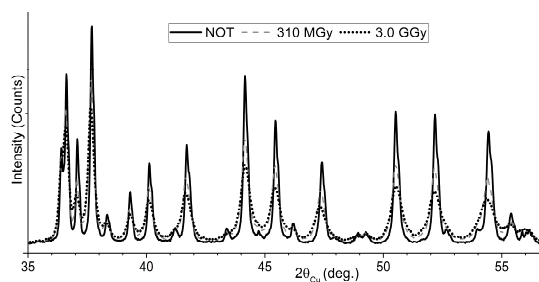


Figure 5. X-Ray diffraction pattern of gibbsite AH₃: before irradiation and after electron irradiation at two doses (310 MGy, 3 GGy).

4. CONCLUSIONS

This study on Portland and Fondu® cements highlights (i) the contribution of hydrates to radiolytic gas production (ii) a significant dependence of the H₂ production on the nature of the hydrates and (iii) a relatively low impact of electron radiations on the structure at least under present irradiation conditions.

ACKNOWLEDGMENTS

This work was performed with financial support of CEA Project « MAD-DEM SPF-AVM ».

Data reported on cement pastes were graciously provided by D. Chartier.

We thank the French EMIR network for supporting this research. We are greatly indebted to B. Boizot and O. Cavani (Ecole Polytechnique, Palaiseau, France) for their help during the irradiations.

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