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Introduction

Arising from spent fuel reprocessing or national defence, nitrates are often encountered in nuclear waste such as decontamination slurries and concentrates. As this kind of waste is often conditioned by solidification in cement-based materials, it is of interest to assess its effect on the radiolytic gas production of cemented wasteforms. Indeed, nitrates are known to have a significant effect on water radiolysis and cement-based materials contain water, both as "free" water in the porosity and "bound" water of the hydrates (calcium silicate hydrates for instance). Water of cement-based materials is known to produce H_2 under irradiation emitted by the waste and previous works report H_2 production drop when nitrates are present in the mixing water. The aim of the present work is to focus on the effect of sodium nitrates on gas production of cement-based materials made of Portland cement with or without addition of blast furnace slag. Indeed, Portland cement is widely used to perform the solidification of nuclear waste and its partial substitution by blast furnace slag is relevant to decrease hydration heat or to improve compatibility with waste such as ion exchange resins.

Experimental

Gamma irradiations (^{60}Co) were performed in the experimental Gammatec facility (Marcoule, France) of STERIS Company. Dose rates between 0.9 to 2 $kGy.h^{-1}$ were applied to achieve total doses of 150 kGy to 20 MGy. Formulations of materials studied in the present work are presented in the following table. All components were weighted and vigorously mixed during five minutes before being cast in 15 mL airtight plastic tubes. Irradiations under argon in sealed glass tubes were performed after 3 months of hydration and post-irradiation gas analysis were performed by gas chromatography. Cement pastes were prepared using Portland cement (SR0 CEM I 52,5N PM supplied by VICAT). Blast furnace slag was supplied by Ecocem France (Fos-sur-Mer plant).

Reference	Type of material	Detailed formulation (wt. ratios unless noted)
P-1	Portland paste without additive	Water/Cement = 0.4
P-2	Portland paste with $NaNO_3$	Water/Cement = 0.4; $NaNO_3$/Cement = 0.0274 ([$NaNO_3$] = 0.8 $mol.L^{-1}$ in the mixing water)
P-3	BFS plus Portland paste without additive	Binder: 15% Portland cement + 85% BFS Water/Binder = 0.4
P-4	BFS plus Portland paste with $NaNO_3$	Binder: 15% Portland cement + 85% BFS Water/Binder = 0.4 $NaNO_3$/Binder = 0.0274 ([$NaNO_3$] = 0.8 $mol.L^{-1}$ in the mixing water)
P-5	Portland paste with CaS	W/C=0.4 ; CaS/Cement = 0.0225
P-6	Portland paste with CaS and NaNO3	W/C=0.4 ; CaS/Cement = 0.0225 ; NaNO3/Cement = 0.0274 ([NaNO3] = 0.8 mol.L-1 in the mixing water)

Results of gamma irradiation

Before assessing the effect of $NaNO_3$ on the mix of Portland plus BFS, the reference case of Portland paste P-2 (water/cement=0.4) containing $NaNO_3$ has been studied for gamma doses from 150 to 600 kGy and compared to the reference Portland paste P-1 without $NaNO_3$. The results presented Figure 1 demonstrate that with the amount of $NaNO_3$ tested (0.8 mol/L in the mixing water, i.e. 1.9%m. $NaNO_3$ in the material), the production of H_2 is strongly reduced of about a factor 10. Nevertheless, it is replaced by an equivalent production of O_2 that comes from direct nitrate radiolysis ($NO_3^- \rightsquigarrow NO_2^- + 1/2O_2$ [1, 2, 3]) and traces of N_2 and N_2O are also detected. Thus, in Portland pastes, the overall radiolytic gas production is slightly increased with $NaNO_3$ which is undesirable considering internal pressurization due to gas build-up of wasteforms.
Considering cement pastes P-3 and P-4 prepared with a binder containing 15 wt.% of Portland cement and 85 wt.% of BFS with a ratio water/binder equal 0.4, the effect of $NaNO_3$ on radiolytic gas production is quite different. Indeed, according to the results presented Figure 2, there is still an important reduction of H_2 production with $NaNO_3$ (P-4) but production of O_2 is very low ($G(O_2) = (6.3 \pm 0.6).10^{-12}$ mol/J) compared to Portland pastes P-2 with $NaNO_3$ ($1.14.10^{-9}$ mol/J, Figure 2). Note that cement paste P-3 without $NaNO_3$ does not produce O_2 just as the simple Portland paste P-1. A weak but significant production of N_2 is observed on cement paste P-4 with $NaNO_3$ ($G(N_2) = (5.0 \pm 0.6).10^{-10}$ mol/J). Other gases containing nitrogen (N_2O and NO) have also been detected but are much lower than N_2 (2% of N_2 maximum) and are not correlated to the dose so that no radiolytic yields have been calculated for these gases. Considering the amount of N_2 produced at 10 MGy, this implies the consumption of 4% of NO_3^- initially present in the materials. Thus, the effect of NO_3^- is expected to be effective for much higher doses, which has been confirmed up to 20 MGy.

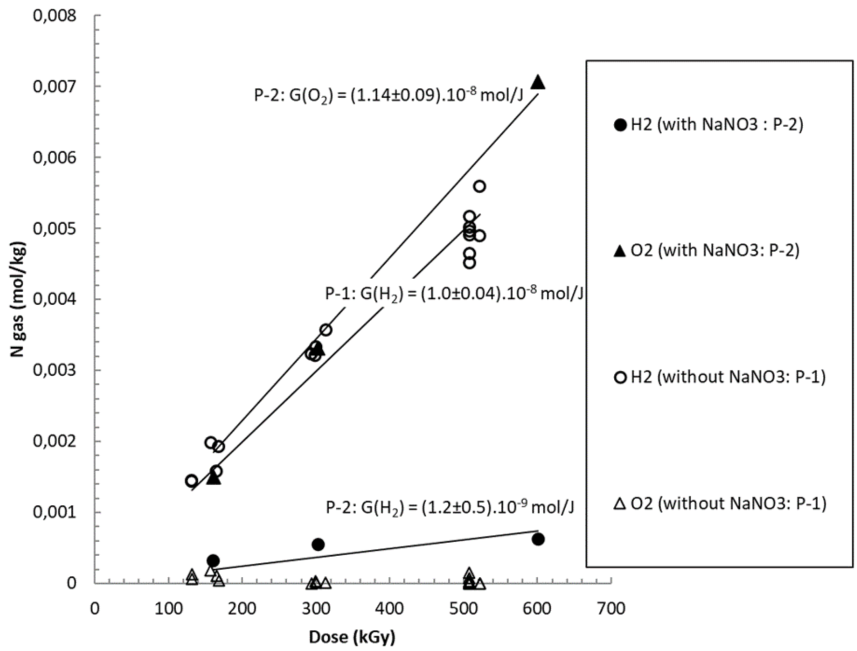

Figure 1. Radiolytic gas production of Portland cement pastes containing (P-2) or not (P-1) $NaNO_3$. Water/Cement = 0.4. $[NaNO_3]$ = 0.8 mol/L in the mixing water of P-2.

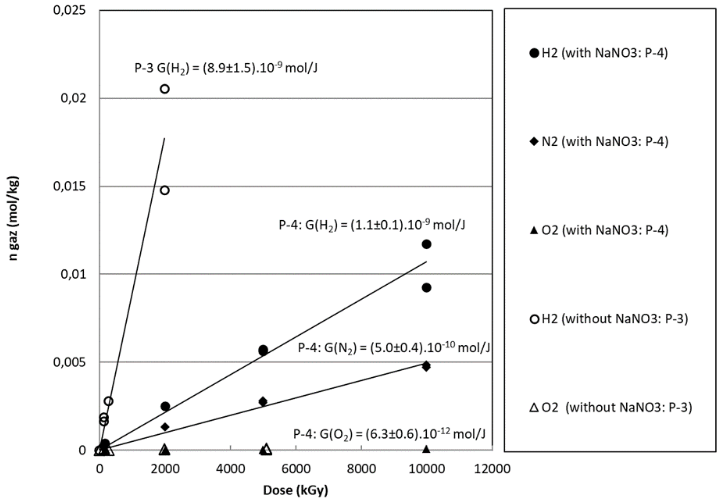

Figure 2. Radiolytic gas production of cement pastes containing (P-4) or not (P-3) $NaNO_3$. Water/Binder = 0.4, Binder: 15% Portland + 85% BFS. [$NaNO_3$]=0.8 mol/L in the mixing water of P-4

The low production of O_2 during gamma irradiation of cement pastes P-4 containing BFS and $NaNO_3$ is probably linked to the presence of sulfide ions (S^{2-}) in the slag (reductive conditions prevail in blast furnace to produce iron). Sulfide ions are thus released in pore solution during hydration of BFS and its partial oxidation into polysulfide radicals S_2^- , S_3^- and S_4^- [4] were responsible for the well-known green-blue coloration of concrete and mortars containing alkali-activated BFS [5]. This coloration remains in anoxic condition that prevails inside materials whereas it disappeared within a few weeks on the surface where atmospheric O_2 is available and drying facilitates its ingress in the material. Thus, it is conceivable that O_2 produced by nitrate radiolysis may be trapped by polysulfide and sulfide oxidation within the material. This assumption is strengthened by the fact that a discoloration is observed after irradiation (Figure 3). Complete discoloration of the cement paste irradiated at high dose (20 MGy) is even observed. Nevertheless, this discoloration is not related to detectable mineralogical changes since X-ray diffraction pattern of the material was not significantly modified by irradiation. As expected for such cement paste [6], C-S-H, hydrotalcite, ettringite and Portlandite are the main phases detected by X-ray diffraction.

Figure 3. Splits of cement pastes P-4 (1 cm by diameter) containing $NaNO_3$ after gamma irradiation (5 and 20 MGy) and reference material (non irradiated).

The involvement of sulfide (which originates from BFS) in the absence of O_2 production under gamma irradiation in the presence of $NaNO_3$ has been strengthened by performing an experiment of addition of calcium sulfide (CaS) to a Portland paste (water/cement = 0.4) containing $NaNO_3$ (P-6) or not (P-5). This addition of CaS to Portland cement without BFS is intended for to mimic sulfide brought by BFS.

With such addition (2.25%m.CaS/cement, which is a representative amount of sulfide in BFS) to Portland paste P-6 containing 2.74%m.$NaNO_3$/cement, no significant O_2 production was noticed whereas H_2 production is lowered compared to the paste P-5 as expected by the occurrence of $NaNO_3$.

Conclusion

$NaNO_3$ strongly affects radiolytic gas production of Portland-based materials (with or without BFS) by reducing H_2 production but other gas are generated: mainly O_2 in the case of pure Portland binder and mainly N_2 in the case of addition of BFS. Reduction of H_2 production due to $NaNO_3$ has also been evidenced under alpha irradiation with mortars containing alpha emitters and results will be published later.

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