



HAL
open science

Effect of sodium nitrate on radiolytic gas production of Portland based materials containing blast furnace slag

David Chartier, Jennifer Sanchez-Canet, Laetitia Bessette, Stéphane Esnouf, Jean-Philippe Renault, Stephen Parraud

► To cite this version:

David Chartier, Jennifer Sanchez-Canet, Laetitia Bessette, Stéphane Esnouf, Jean-Philippe Renault, et al.. Effect of sodium nitrate on radiolytic gas production of Portland based materials containing blast furnace slag. NUWCEM 2022 - 4th International Symposium on Cement-Based Materials for Nuclear Wastes, May 2022, Avignon, France. cea-03773977

HAL Id: cea-03773977

<https://cea.hal.science/cea-03773977>

Submitted on 23 Sep 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Effect of sodium nitrate on radiolytic gas production of Portland based materials containing blast furnace slag

D. Chartier^{1*}, J. Sanchez-Canet¹, L. Bessette², S. Esnouf³, J-P. Renault⁴, S. Parraud⁵

1 CEA, DES, ISEC, DE2D, Univ Montpellier, Marcoule, France.

2 Vicat, 4, Rue Aristide Bergès, F-38080 L'Isle d'Abeau, France

3 CEA, DES, DPC, SECR, F-91191, Gif-sur-Yvette, France.

4 Université Paris Saclay, CEA, CNRS, NIMBE, F-91191, Gif-sur-Yvette, France

5 CEA, DES, DFDE, SECC, F-13108, St Paul lez Durance, France.

*Corresponding Author, E-mail: david.chartier@cea.fr

KEYWORDS: radiolysis, nitrate, H₂, cement, Portland, blast furnace slag, waste

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 wastefoms. 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 H₂ under irradiation emitted by the waste and previous works report H₂ 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 (⁶⁰Co) 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 NaNO ₃	W/C=0.4 ; CaS/Cement = 0.0225 ; NaNO ₃ /Cement = 0.0274 ([NaNO ₃] = 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 ($\text{NO}_3^- \rightsquigarrow \text{NO}_2^- + 1/2\text{O}_2$ [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 wastefoms.

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 ($G(\text{O}_2) = (6.3 \pm 0.6) \cdot 10^{-12}$ mol/J) compared to Portland pastes P-2 with NaNO_3 ($1.14 \cdot 10^{-9}$ 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 ($G(\text{N}_2) = (5.0 \pm 0.6) \cdot 10^{-10}$ 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.

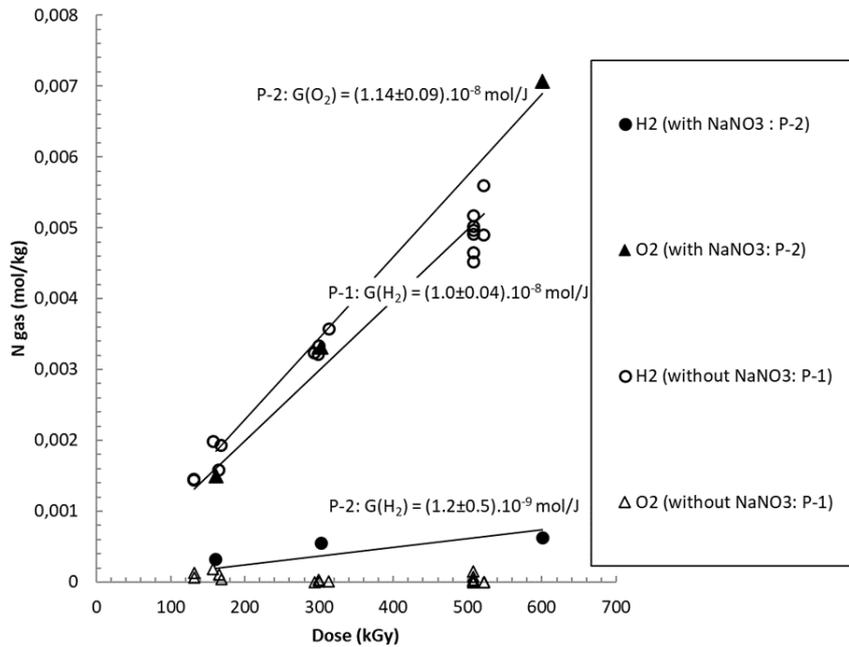


Figure 1. Radiolytic gas production of Portland cement pastes containing (P-2) or not (P-1) NaNO_3 . Water/Cement = 0.4. $[\text{NaNO}_3] = 0.8$ mol/L in the mixing water of P-2.

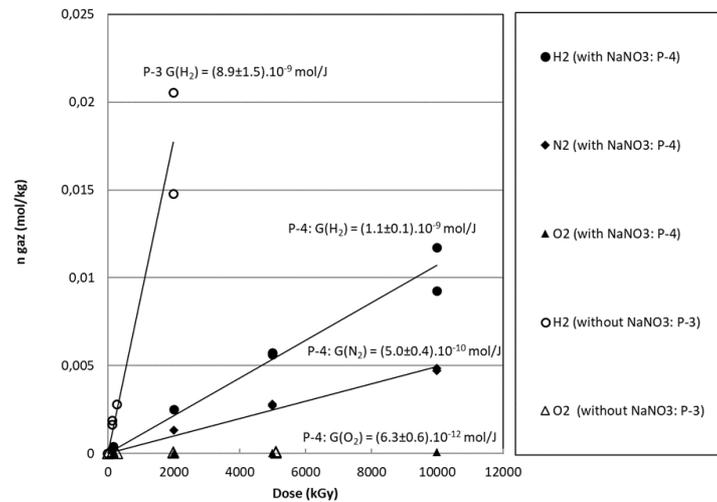


Figure 2. Radiolytic gas production of cement pastes containing (P-4) or not (P-3) NaNO₃. Water/Binder = 0.4, Binder: 15% Portland + 85% BFS. [NaNO₃]=0.8 mol/L in the mixing water of P-4

The low production of O₂ during gamma irradiation of cement pastes P-4 containing BFS and NaNO₃ is probably linked to the presence of sulfide ions (S²⁻) 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 S₂⁻, S₃⁻ and S₄⁻ [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 O₂ is available and drying facilitates its ingress in the material. Thus, it is conceivable that O₂ 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 NaNO₃ after gamma irradiation (5 and 20 MGy) and reference pastes (non irradiated).

The involvement of sulfide (which originates from BFS) in the absence of O₂ production under gamma irradiation in the presence of NaNO₃ has been strengthened by performing an experiment of addition of calcium sulfide (CaS) to a Portland paste (water/cement = 0.4) containing NaNO₃ (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*.NaNO₃/cement, no significant O₂ production was noticed whereas H₂ production is lowered compared to the paste P-5 as expected by the occurrence of NaNO₃.

Conclusion

NaNO₃ strongly affects radiolytic gas production of Portland-based materials (with or without BFS) by reducing H₂ production but other gas are generated: mainly O₂ in the case of pure Portland binder and mainly N₂ in the case of addition of BFS. Reduction of H₂ production due to NaNO₃ has also been evidenced under alpha irradiation with mortars containing alpha emitters and results will be published later.

Acknowledgments

This work was supported by Andra as part of the program “Investissements d’Avenir” launched by the French government (MATRICE project). The authors are grateful to V. Labed, M. Charlot, K. Ressaire, L. Berthillot, S. Lutzler, L. Karafotis for their contribution to gamma and alpha irradiations. Gamma irradiation were performed in the irradiator Gammatec of STERIS Company located on the Marcoule site.

[¹] M. L. Hyder, « The Radiolysis of Aqueous Nitrate Solutions », The Journal of Physical Chemistry, Volume 69, Number 6 June 1966.

[²] H. Bernhard Pogge, F. T. Jones, « The Effects of Temperature and Additives in the Radiolysis of Potassium Nitrate », The Journal of Physical Chemistry, Volume 74, Number 8 April 18, (1970), 1700-1705.

[³] P.Y. Jiang « Gamma radiolysis study of concentrated nitric acid solutions », J. Chem. Soc. Faraday Trans., 90 (1994), pp. 93–95.

[⁴] T. Chivers, P. J. W. Elder, « Ubiquitous trisulfur radical anion: fundamentals and applications in materials science, electrochemistry, analytical chemistry and geochemistry », Chem. Soc. Rev., 2013, 42, 5996-6005.

[⁵] D. Le Cornec, Q. Wang, L. Galois, G. Renaudin, L. Izoret, G. Calas, « Greening effect in slag cement materials », Cement and Concrete Composites, 84 (2017) 93-98.

[⁶] S. Stephant, Étude de l’influence de l’hydratation des laitiers sur les propriétés de transfert gazeux dans les matériaux cimentaires, Ph.D. Thesis, University of Bourgogne, France (2015)