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# Novel Portland cement matrices incorporating a gamma -MnO<sub>2</sub> /Ag<sub>2</sub>O hydrogen/tritium getter -structure changes and trapping performance

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1 **Novel Portland cement matrices**  
2 **incorporating a  $\gamma$ -MnO<sub>2</sub>/Ag<sub>2</sub>O hydrogen/tritium getter -**  
3 **Structure changes and trapping performance**

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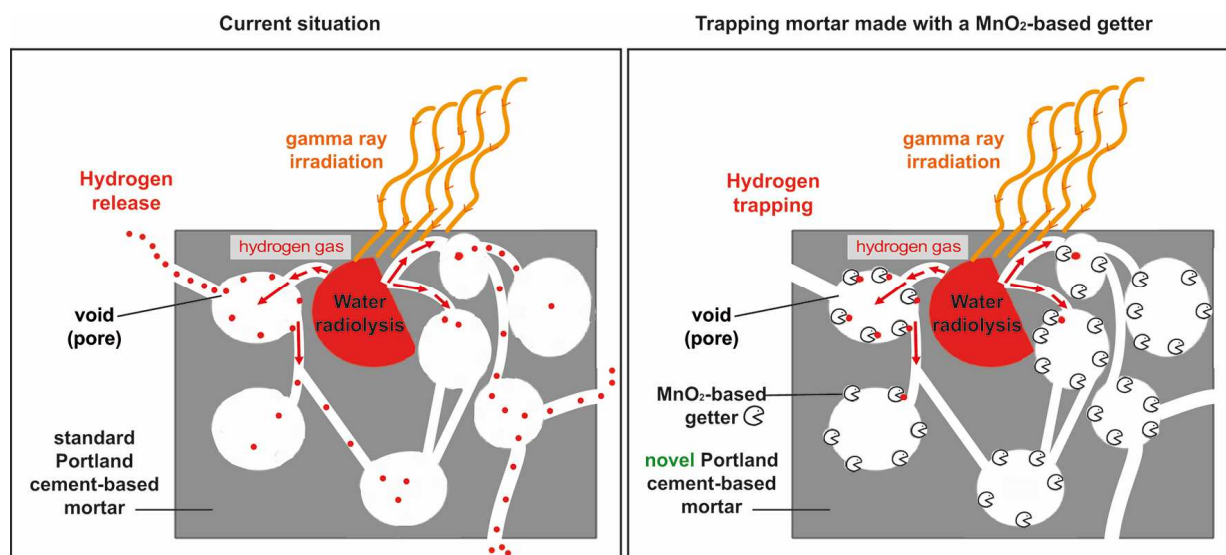
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11 **Graphical Abstract:**



12  
13

## 1 **Abstract**

2 This study investigates novel Portland cement-based mortars, developed for  
3 hydrogen/tritium trapping and radioactive waste immobilization. They incorporate a  $\gamma$ -  
4  $\text{MnO}_2/\text{Ag}_2\text{O}$  getter powder at 10% wt (i.e. 6.8 to 7.1% vol). Compared to former patented  
5 materials, no drying or heat treatment of the materials is needed.

6 Complementarily to X Ray Diffractometry (XRD) and thermo-gravimetry analysis (TGA),  $^{27}\text{Al}$   
7 and  $^{29}\text{Si}$  Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR) evidences that the  
8 structure of the Portland cement solids (i.e. the C-A-S-H) is not impacted by the presence of  
9 getter, even after several month curing. Yet, Scanning Electron Microscopy coupled to  
10 Energy Dispersive Spectroscopy (SEM+EDS) shows that calcium is significantly present at the  
11 surface of the getter grains; this could affect trapping efficiency.

12 However, after gamma irradiation with cumulated doses of 491 or 997 kGy (i.e. 23 to 46  
13 days at  $900 \text{ Gy}\cdot\text{h}^{-1}$ ), all mortars made with getter have a hydrogen trapping efficiency of  
14 between 77 and 96%, when compared to the irradiation of mortars made with a non-  
15 trapping  $\gamma\text{-MnO}_2$  powder, or to the irradiation of pure water considered alone.

16 This means that the developed mortars display excellent hydrogen trapping efficiency,  
17 without any impact on their solid structure.

18

19 **Keywords:** Portland cement; radioactive waste; trapping; tritium; getter; Hydrogen fires and  
20 explosions; Hydrogen suppression

21

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# 1 Introduction

## 2 1.1 Industrial context

3 In a number of industrialized countries, particularly in the USA and in France,  
4 significant amounts of the electrical energy supply are provided by the nuclear industry,  
5 which uses the nuclear fission of  $^{235}\text{U}$  in pressurized or boiling water reactors <sup>1</sup>. Due to this  
6 activity, radioactive waste is generated every year, with 90.9 %vol short-lived and very low  
7 (to low) activity compounds [ANDRA 2009, ANDRA 2018].

8 Currently, the safe conditioning of these hazardous waste includes  
9 stabilization/solidification in Portland cement-based materials, which are a robust and  
10 economically viable solution [Ojavan 2005, Shi 2006, AIEA2007, LeCaer 2017]. Alternatives  
11 exist for specific applications, where Portland cements are inadequate, e.g. magnesium  
12 potassium phosphate cements or calcium aluminate phosphate cements for the  
13 immobilization of aluminum [Kinoshita 2013, CauDitCoumes 2014, Wang 2020], and  
14 geopolymers for the solidification/stabilization of organic liquids [Cantarel 2015, Davy 2018]  
15 or magnesium alloys [Lambertin 2012].

16 Nuclear radioactive wastes are radiation emitters of various energy and type. Their  
17 ionizing rays (of either  $\alpha$ ,  $\beta$  or  $\gamma$  type) interact with the surrounding water (from the disposal  
18 site or from the cement conditioning matrix), generating hydrogen (and other products) due  
19 to a range of radiolysis reactions [Bouniol 2008; Varlakov 2021]. Hydrogen gas may also be  
20 released by metal corrosion in the alkaline porewater of Portland-cement materials  
21 [CauDitCoumes 2014]. Whenever hydrogen gas is released by a radioactive (and/or metallic)

---

<sup>1</sup> According to the International Energy Agency, in 2019 in the US, an amount of 843 330 GWh electricity has been produced from nuclear power (it is the 3<sup>rd</sup> electrical energy source, with 1,634,595 GWh from natural gas and 1,058,637 GWh from coal), see :  
<https://www.iea.org/data-and-statistics/data-tables?country=USA&energy=Electricity&year=2019>.

1 waste immobilized in a cement matrix, its pressure may build up and eventually reach the  
2 4 %vol flammability limit in air [Murugesan 2013] associated to an ignition energy of only  
3 0.03 mJ [Zhong 2014, Wang 2020], so that the triggering conditions for hydrogen explosion  
4 may be easily satisfied. Hydrogen release can thus raise important safety issues. This justifies  
5 strict regulations concerning the gas release of cemented waste packages sent to disposal  
6 [Lambertin 2010].

7 Apart from hydrogen gas, tritium gas, an isotope of hydrogen of 3 amu, is released by wastes  
8 from current fission nuclear reactors, and significantly more will be produced in the near  
9 future by the nuclear fusion reactor ITER. The latter is under construction in France by a  
10 worldwide collaboration spanning 35 countries [ANDRA 2018, ASN 2010].

11

12 In France, the authorized radioactive waste repositories are managed by ANDRA  
13 (Agence Nationale pour la gestion des Déchets RAdioactifs). For the main CSA near-surface  
14 repository (Soulaines-Dhuys, Aube), current specifications limit the tritium outgassing rate of  
15 waste packages below 2.105 Bq per ton of package and per day, considering all possible  
16 gaseous forms of tritium [ANDRA 2015]. This is so restrictive that in practice, most tritiated  
17 waste packages are excluded from the CSA repository, and currently stored in interim  
18 facilities. Tritiated waste need to be accepted for repository in greater amounts than what is  
19 currently feasible. This situation is similar to that of other industrialized countries managing  
20 tritiated waste.

## 21 **1.2 Scientific background**

22 Although cement-based matrices are a viable option for the immobilization of  
23 hydrogen or tritium-releasing nuclear waste, without peculiar precautions, and whatever  
24 their formulation, they release significant amounts of H<sub>2</sub> gas (and other radiolytic products)

1 under varied ionizing rays, due to radiolysis reactions [Mockel1982, Bouniol 2008,  
2 LeCaer2017, Acher 2018, Chartier2018, Varlakov 2021]. The international patent [Lambertin  
3 2010] shows that significant trapping of H<sub>2</sub> is possible in cement matrices, provided that they  
4 include a dedicated hydrogen-tritium getter.

5 This getter is a mix of  $\gamma$ -MnO<sub>2</sub> and Ag<sub>2</sub>O, aimed at irreversibly trapping gaseous H<sub>2</sub> [Kozawa  
6 1980, Kozawa 1981a, Kozawa 1981b, Galliez 2012] and its isotopes (deuterium and tritium  
7 forms). Unlike other hydrogen scavengers such as polymeric compounds, metal hydrides or  
8 oxides [Nigrey 2000, Chaudron 1998, Lambertin 2010], the  $\gamma$ -MnO<sub>2</sub>/Ag<sub>2</sub>O getter is neither  
9 pyrophoric (i.e. with a high inflammation risk) nor sensitive to ionizing rays [Lousot 2006;  
10 Chlique 2015]. Apart from hydrogen, independent research has proven its ability to trap  
11 tritium gas [Janberg 1995].

12 Like other getter and trapping sorbent types [Asmussen 2018, Martin 2019], the  $\gamma$ -  
13 MnO<sub>2</sub>/Ag<sub>2</sub>O getter may be incorporated in cement-based matrices. [Lambertin 2010]  
14 describe a pure Portland-cement based paste incorporating the  $\gamma$ -MnO<sub>2</sub>/Ag<sub>2</sub>O getter, but  
15 requiring 60°C drying. Despite excellent trapping performance (120 cm<sup>3</sup>/g after 40 days  
16 under pure H<sub>2</sub> compared to 196 cm<sup>3</sup>/g for the dry getter considered alone), this thermal  
17 treatment makes the cement matrix difficult to implement at the industrial scale relevant for  
18 nuclear waste disposal.

19 Although the best trapping performance of the  $\gamma$ -MnO<sub>2</sub>/Ag<sub>2</sub>O mix is achieved in the dry state  
20 [Kozawa 1981b], in proportions of 87 %wt  $\gamma$ -MnO<sub>2</sub> / 13 %wt Ag<sub>2</sub>O [Galliez 2015], significant  
21 trapping is also achieved in the partially water-saturated state. For instance, in [Kozawa  
22 1981b], for the same  $\gamma$ -MnO<sub>2</sub>/Ag<sub>2</sub>O mix, 22 cm<sup>3</sup> H<sub>2</sub> are trapped when the mix includes 20%  
23 water, compared to 39 cm<sup>3</sup> H<sub>2</sub> trapped by a mix dried at 75°C.

### 24 1.3 Aims and scopes

1 For a safe disposal of hydrogen- or tritium- generating radioactive waste, it is  
2 compulsory to have cement-based matrices 1) adapted to immobilize hydrogen or tritium-  
3 releasing waste, i.e. (for instance) incorporating the  $\gamma$ -MnO<sub>2</sub>/Ag<sub>2</sub>O getter, and 2) adapted to  
4 industrial uses, i.e. not requiring any heat treatment and compliant with ANDRA industrial  
5 specifications.

6 In earlier research [Lanier 2020], such mortars have been designed based on pure and  
7 composed Portland cements (Type I and Type V). They incorporate a fixed amount of 10%  $\gamma$ -  
8 MnO<sub>2</sub>/Ag<sub>2</sub>O getter in a powdered form (expressed in % of the total mortar mass). Their  
9 curing is endogenous, and no heat treatment is performed.

10 The trapping efficiency of these novel developed mortars is assessed in this study,  
11 because of potential detrimental interactions between the  $\gamma$ -MnO<sub>2</sub>/Ag<sub>2</sub>O getter and the  
12 Portland cement paste (mainly the porewater and the Calcium Aluminate and Silicate  
13 Hydrates i.e. the C-A-S-H<sup>2</sup>, see [Geng 2017]). In particular, a significant cation sorption on  $\delta$ -  
14 MnO<sub>2</sub>, such as Ca<sup>2+</sup>, has been identified by [Pretorius 2001]. This phenomenon, if occurring  
15 for the  $\gamma$ -MnO<sub>2</sub>/Ag<sub>2</sub>O getter present in the partially water-saturated Portland cement-based  
16 mortars, may significantly hinder their hydrogen trapping efficiency.

17 Following the promising mortars developed in [Lanier 2020], this contribution  
18 investigates first, what interactions exist between the  $\gamma$ -MnO<sub>2</sub>/Ag<sub>2</sub>O getter and the Portland  
19 cement solids or its porewater, by combining (1) X Ray Diffraction (XRD), thermogravimetry

---

<sup>2</sup> For the sake of simplicity, in this research, the main solid components of hydrated Portland-based cements, which incorporate calcium silicates, are referred to as C-A-S-H (Calcium Aluminate and Silicate Hydrates), but in pure Portland (Type I) cement, aluminates are almost absent, so that a more adequate term would be Calcium Silicate Hydrates (C-S-H). However, there are actual C-A-S-H in composed Portland cements, such as in the Type V also used herein.



1 (TGA) analysis,  $^{27}\text{Al}$  and  $^{29}\text{Si}$  Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR)  
2 for the interactions between the cement solids and the getter, and (2) SEM/EDS (Scanning  
3 Electron Microscopy/Energy Dispersive Spectroscopy) of the getter powder embedded in a  
4 hardened mortar.

5 Secondly, the  $\text{H}_2$  trapping performance is investigated for the novel mortars incorporating  
6 the  $\gamma\text{-MnO}_2/\text{Ag}_2\text{O}$  getter, and compared to mortars made with non-trapping  $\gamma\text{-MnO}_2$  only.

7 Gamma Ray irradiation experiments are performed on mortar samples placed in an inert  
8 argon gas atmosphere, after 4 months curing and without preliminary drying or heat  
9 treatment. Gamma Ray irradiation generates *in situ* radiolysis of the water present in the  
10 mortars [Acher 2018]. This in turn creates mainly hydrogen gas, that the getter may or may  
11 not trap. Finally, SEM observations and nitrogen sorption-desorption measurements are  
12 performed before and after irradiation, in order to analyze the changes in the mortar  
13 structure.

14

## 2 Materials and Methods

### 2.1 Materials

#### 2.1.1 Raw powders

All materials are made either with Type I (pure) Portland cement or with Type V (composed) Portland cement. Detailed cement references are given in Appendix A.1. According to its technical specifications, Type V cement is a mix of 53% clinker, 3% gypsum, 22% fly ash and 22% blast furnace slag. Contrarily to Type I cement, the pozzolanic and hydraulic supplementary materials (i.e. fly ash and blast furnace slag) of Type V cement avoid cement paste carbonation [Baroghel-Bouny 1994]. The chemical composition of both cements, determined by X Ray Fluorescence (XRF), is given in Table 1. Their particle size distribution (PSD) is given in Fig. 1, and shown to be similar to that of  $\gamma$ -MnO<sub>2</sub> and  $\gamma$ -MnO<sub>2</sub>/Ag<sub>2</sub>O getter. These PSD are determined by morpho-granulometry on a MorphologiG3 apparatus (Malvern Panalytical, Netherlands and UK).

Mortars are made by using specifically designed grain size classes of a standard pure silica sand (see Appendix A.1. for more information).

The  $\gamma$ -MnO<sub>2</sub>/Ag<sub>2</sub>O getter is provided by A3I (France). A commercial Manganese (IV) oxide  $\gamma$ -MnO<sub>2</sub> powder is used (reference n. 8.05958.1000, Merck, USA). Although it is slightly finer,  $\gamma$ -MnO<sub>2</sub> has a particle size distribution close to that of the  $\gamma$ -MnO<sub>2</sub>/Ag<sub>2</sub>O powder (Fig. 1). With the selected mortar formulations,  $\gamma$ -MnO<sub>2</sub> is used as a non-trapping powder, in order to quantify (by comparison) the trapping performance of mortars incorporating the  $\gamma$ -MnO<sub>2</sub>/Ag<sub>2</sub>O getter, without changing the mortar microstructure. From XRF measurements,

1 Table 1 shows the high purity of  $\gamma$ -MnO<sub>2</sub> and  $\gamma$ -MnO<sub>2</sub>/Ag<sub>2</sub>O powders. More elements on  
2 powder and sand characterization are given in Appendix A.1.

### 3 2.1.2 Mortars and pastes

#### 4 2.1.2.1- Reference material

5 The Portland cement paste described in [Lambertin 2010], labelled PASTE-REF-CEMI, is made  
6 with a composition given in Table 2. Details on its manufacturing process and curing  
7 conditions are given in Appendix A.1.

#### 8 2.1.2.2- Hydrogen trapping mortars

9 For formulation and characterization purposes, unless otherwise stated,  $\gamma$ -MnO<sub>2</sub> is used  
10 instead of the more expensive  $\gamma$ -MnO<sub>2</sub>/Ag<sub>2</sub>O getter. The getter powder is only mixed in  
11 mortars for the gamma irradiation experiments and SEM observations (see below).

12 Two mortars are labelled TER-, meaning that they incorporate two main grain size classes of  
13 silica sand and powdered  $\gamma$ -MnO<sub>2</sub> (or  $\gamma$ -MnO<sub>2</sub>/Ag<sub>2</sub>O); they mainly differ by the cement nature  
14 (Type I or Type V) and the W/C ratio; they are labelled TER-I 54 TER-V-48 (where I or V  
15 stands for the type of cement, and 54 or 48 is the water-to-cement ratio W/C multiplied by  
16 one hundred).

17 A third formulation is labelled QUAT-V-48 (where V stands for Type V cement and 48 is a  
18 hundred times the W/C ratio), for quaternary mortar. In that case, apart from incorporating  
19 two grain classes of silica sand, the ( $\gamma$ -MnO<sub>2</sub> or  $\gamma$ -MnO<sub>2</sub>/Ag<sub>2</sub>O) powder is partially used after a  
20 granulation step. The granules are a mix of cement, powder and water; they are  
21 manufactured, subjected to endogenous curing for 7 days and selected (by sieving) for their  
22 size; granules display significant porosity, which increases the pore volume available to gas.

1 In order to fulfill the industrial specifications, the  $\gamma$ -MnO<sub>2</sub> (or  $\gamma$ -MnO<sub>2</sub>/Ag<sub>2</sub>O) is used both as  
2 granules and powder in the QUAT-V-48 formulation.

3 The composition of the three developed trapping mortars and their fresh state properties  
4 (spread and Vicat setting time) are given in Table 2. Note that all three mortars contain very  
5 close water proportions and identical  $\gamma$ -MnO<sub>2</sub> (or  $\gamma$ -MnO<sub>2</sub>/Ag<sub>2</sub>O) amounts. A 10% mass  
6 proportion of  $\gamma$ -MnO<sub>2</sub> (or  $\gamma$ -MnO<sub>2</sub>/Ag<sub>2</sub>O) corresponds to 6.8 to 7.1% of the mortar total  
7 volume depending on the formulation considered (Table 2). This means that no percolation-  
8 type cluster, expected from 15% vol, may develop and change the wasteform properties  
9 [Juoi 2008, Ojovan 2005].

10 The W/C ratio for each mortar is chosen as the smallest possible while complying with the  
11 industrial specifications (in particular, a minimum ASTM spread of 20 cm), while maximizing  
12 compressive strength and minimizing fluid transport properties.

### 13 2.1.2.3- Mortar manufacturing and maturation

14 For all mortars, the mixing procedure is carried out in accordance with standard EN 196-1.  
15 For pore structure assessment, cylindrical molds of 65 mm by diameter and 10-15 mm by  
16 height are filled with fresh mortar, sealed and cured at ambient temperature (21°C +/-1) for  
17 127 days (4 months and a half). This duration is chosen in order to have a maturation close  
18 to that of samples subjected to irradiation tests (see Table 3).

19 For gamma irradiation tests, reference mortars are made with  $\gamma$ -MnO<sub>2</sub> powder or with a mix  
20 of  $\gamma$ -MnO<sub>2</sub> powder and granules, for the three formulations TER-I 54, TER-V 48 and QUAT-V  
21 48. Hydrogen trapping mortars with the same formulations are made using  $\gamma$ -MnO<sub>2</sub>/Ag<sub>2</sub>O  
22 getter. For each formulation and powder type ( $\gamma$ -MnO<sub>2</sub> or getter), four samples are made by  
23 pouring the fresh paste into sealed tubes of 15 mL, corresponding to an individual sample

1 mass of 22.5 g +/-1.4. After endogenous curing at ambient temperature (21°C +/-1), gamma  
2 Ray irradiation starts after 115-118 days (i.e. 4 months) maturation, and ends at an age of  
3 138-164 days (i.e. 5-6 months) depending on the cumulated dose applied (Table 3).

#### 4 2.1.2.4- Paste manufacturing, curing and drying

5 In order to avoid the shadowing effects of sand presence, chemical characterizations are  
6 performed on Type I and Type V cement pastes made at W/C=0.50 and 0.54 (for Type I  
7 cement) and 0.48 and 0.50 (for Type V cement). Using a common W/C=0.50 allows more  
8 accurate comparison between Type I and Type V cement pastes than only 0.54 or 0.48 (used  
9 for the mortars).

10 For XRD, TGA and MAS NMR experiments, after 127 days (i.e. 4,5 months) endogenous  
11 curing at a constant ambient temperature of 21°C +/-1, each paste sample is dried by the  
12 solvent exchange technique (with isopropanol) [Konecny 1993; Korpa 2006; Zhang and  
13 Scherer 2011; Stephant 2015; Lahalle 2016] and powdered manually using a mortar and  
14 pestle. Further details on paste preparation prior to characterization tests are provided in  
15 Appendix A.1.

16 The age and characteristics of the irradiated samples is given in Table 3. The samples tested  
17 after irradiation by nitrogen sorption-desorption and SEM are those retrieved after the  
18 irradiation experiment (Table 6); their age is that given in Table 3 (i.e. 138-164 days  
19 depending on the cumulated dose).

## 1 2.2 Characterization methods

2 For each mortar, classical protocols are used to characterize their pore size distribution and  
3 porosity, before and/or after irradiation (nitrogen sorption-desorption isotherms, ethanol  
4 saturation). These are detailed in Appendix A.2. With these methods, different non  
5 irradiated (NI) and irradiated (IR) mortar samples are characterized at the same age.

6 The procedure for Scanning Electron Microscopy (SEM) observations of the mortars is also  
7 described in Appendix A.2.

### 8 2.2.1 Structure characterization of the cement pastes

9 Cement paste characterization includes thermogravimetry analysis (TGA). Its protocol is  
10 given in Appendix A.2.

#### 11 2.2.1.1- XRD analysis

12 Qualitative diffraction data are collected at room temperature with a Bragg-Brentano  
13 diffractometer in the  $\theta/\theta$  geometry (Bruker Advance D8 type), equipped with a lynx-eye  
14 detector, and using copper Cu  $K\alpha_1$  and  $K\alpha_2$  radiations ( $\lambda = 1.54060$  and  $1.54440$  Å, at 40.0 kV  
15 and 40.0 mA), in the  $2\theta$  range from 10 to 70°, with 0.03° steps and 4 s acquisition time per  
16 step. The energy discrimination of the detector is adapted in order limit fluorescence (due to  
17 the presence of Mn in the specimens).

#### 18 2.2.1.2- MAS NMR measurements

19 For  $^{29}\text{Si}$ , the experiments are performed at a Larmor frequency of 79.5 MHz, on a 9.4 T  
20 Bruker Avance 400 MHz spectrometer. In order to identify the silicate  $Q^n$  speciation (where n  
21 is the number of bridging oxygen atoms of the silicate under investigation),  $^{29}\text{Si}$  MAS-NMR  
22 spectra are recorded on a 7 mm probe head with a spinning frequency ( $n_{\text{rot}}$ ) of 5 kHz, a 6  $\mu\text{s}$   
23 pulse length (and 90° pulse angle), 128 to 1400 transients (depending on the sample

1 considered) and an optimized recycle delay (rd) of 20 s (D1). The <sup>29</sup>Si chemical shifts are  
2 referred to a TetraMethylSilane (TMS) solution as 0 ppm value.

3 <sup>27</sup>Al spectra are acquired on a Bruker Avance II 800 MHz (18.8 T) apparatus at a Larmor  
4 frequency of 208.5 MHz, with a 3.2 mm zircon probe head. The spinning frequency is of  
5 22 kHz, the pulse length of 0.55 μs, the pulse angle of π/10, the optimized recycle delay of 1  
6 s (D1), and the number of transients is of 2048. The <sup>27</sup>Al chemical shifts are calibrated with a  
7 Al(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup> solution.

8 After acquisition, all spectra are decomposed using the DMFIT software [Massiot 2002]. This  
9 provides the relative proportions of the different components of the spectra, particularly of  
10 the Q<sup>n</sup> silicate units (where n varies between 1 and 4, with or without Al substitutions).

11 For the <sup>29</sup>Si spectra, the mean C-A-S-H chain length is calculated according to [Richardson  
12 1999]:

$$13 \quad MCL = \text{Mean Chain Length} = [2 * (Q^1 + Q^2 + \frac{3}{2} * Q^2(Al))] / Q^1$$

14 The (Al/Si) molar ratio of the C-A-S-H, i.e. the substitution rate of silicates by aluminates, is  
15 also calculated using [Richardson 1994], [Andersen 2004] as:

$$16 \quad Al/Si = \frac{1}{2} Q^2(Al) / (Q^1 + Q^2 + Q^2(Al))$$

### 17 2.2.2 Hydrogen trapping performance: *in situ* gamma irradiation experiments

18 In this research, prior to irradiation, each sample is sealed in a glass vial under an inert argon  
19 atmosphere, at a pressure slightly smaller than atmospheric pressure. No interaction with  
20 ambient air exists.

1 Gamma irradiation experiments generate *in situ*, i.e. within the mortars, a number of  
2 radiolytic products, including gaseous H<sub>2</sub> mainly from the free or bound water present, due  
3 to water radiolysis [Bouniol 2008; Acher 2018]. Whenever the  $\gamma$ -MnO<sub>2</sub>/Ag<sub>2</sub>O getter is  
4 present, it is expected that H<sub>2</sub> is irreversibly trapped and less gas is released from the  
5 mortars. Other gases may also be produced, mainly O<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub> or N<sub>2</sub>, e.g. due to super-  
6 plasticizer degradation under gamma ray action [Chartier 2018].

7 The protocol for external gamma irradiation is presented in Fig. 2. It is identical to that  
8 described in [Chartier 2018]. All experiments are performed at room temperature, with an  
9 average dose rate of 900 Gy.h<sup>-1</sup> and an integrated dose of 491.2 or 997.5 kGy. This  
10 represents 23 or 46 days of gamma ray irradiation. All samples are monoliths (i.e. not  
11 crushed or powdered mortars). Two different samples per dose and per mortar formulation  
12 (either made with  $\gamma$ -MnO<sub>2</sub> or with  $\gamma$ -MnO<sub>2</sub>/Ag<sub>2</sub>O) are tested. The greatest cumulated dose  
13 corresponds to the order of magnitude of the dose in [Mobasher 2015] (4.77 MGy over 11  
14 days) for a slag cement-based grout used for encapsulation of low and intermediate level  
15 radioactive waste. Further details on the test set-up and gas measurement apparatus are  
16 given in Appendix A.3.

17 From the raw measurement of gas volume percentage in the airtight test vial (%*vol*) (by gas  
18 micro-chromatography), the amount of gas  $n(\text{gas})$  (in mol) is deduced from the gas perfect  
19 law, and the corresponding gas radiolytic yield of the considered sample  $G(\text{gas})_{\text{material}}$  is  
20 calculated (see Appendix A.3.). In this research, only nitrogen gas is detected together with  
21 H<sub>2</sub>. Due to the amounts produced, only  $G(\text{H}_2)_{\text{material}}$  is discussed. The radiolytic yield for  
22 other produced gaseous species is not accounted for.



1 Because water is the main significant source of H<sub>2</sub> in the mortars, the hydrogen radiolytic  
 2 yield is rather expressed (in mol/J) after being normalized by the mass water fraction  $w_{water}$   
 3 as:

$$4 \quad \frac{G(H_2)_{material}}{w_{water}} = \frac{n(H_2)}{D m_{total\ water}}$$

5 Where  $w_{water} = m_{total\ water}/m$  and  $m_{total\ water}$  is the total water mass inside the sample,  
 6 both free and bound;  $m$  is the sample mass.

7 The measurements are generally compared to the radiolytic yield of free water. It is not easy  
 8 to assess this value experimentally because H<sub>2</sub> recombines easily to form water molecules  
 9 [LaVerne 2009; Chartier 2017]. In presence of H<sub>2</sub> trapping compounds (such as Br<sup>-</sup> ions),  
 10 [LaVerne 2009] determined a radiolytic yield for free water at a value of  $4.46 \times 10^{-8}$  mol/J.  
 11 This value is used as a reference (labelled free or pure water) in this research.

12 The amount of H<sub>2</sub> generated by free water is a theoretical value  $n(H_{2\ free\ water})$  (expressed  
 13 in mol). It is calculated using the actual amount of water present in each mortar formulation  
 14 (i.e. both free and bound water), as in [Chartier 2017], by:

$$15 \quad n(H_{2\ free\ water}) = G(H_2)_{water} \times D \times m_{water}$$

16 Where  $G(H_2)_{water} = 4.46 \times 10^{-8}$  mol/J [LaVerne 2009];  $D$  is the integrated dose (491.2 or  
 17 997.5 kGy) and  $m_{water}$  is the total water mass (expressed in kg) present in the sample  
 18 considered.

19 Finally, a first trapping efficiency parameter  $TE_{free\ water}$  (expressed in % mol trapped H<sub>2</sub>) is  
 20 deduced, by comparison with free water hydrogen production, as:

$$21 \quad TE_{free\ water} = 100 \times \frac{n(H_{2\ free\ water}) - n(H_{2\ mortar\ with\ getter})}{n(H_{2\ free\ water})}$$

1 Where  $n(H_{2 \text{ mortar with getter}})$  is the amount (in mol) of H<sub>2</sub> released by the mortar made  
2 with getter. If no H<sub>2</sub> is released by a mortar made with getter compared to free water, the  
3 corresponding value of  $TE_{free \text{ water}}$  is 100%.

4 A second trapping efficiency parameter is also deduced by comparing the amounts of H<sub>2</sub>  
5 released by MnO<sub>2</sub>-added mortars and getter-added mortars (with the same formulation), as:

$$6 \quad TE_{relative \text{ to } MnO_2} = 100 \times \frac{n(H_{2 \text{ MnO}_2}) - n(H_{2 \text{ getter}})}{n(H_{2 \text{ MnO}_2})}$$

7 Where  $n(H_{2 \text{ MnO}_2})$  is the amount of H<sub>2</sub> produced by the  $\gamma$ -MnO<sub>2</sub>-added mortar (in mol) and  
8  $n(H_{2 \text{ getter}})$  is the amount of H<sub>2</sub> produced by the getter-added mortar (in mol). As with  
9  $TE_{free \text{ water}}$ , if no H<sub>2</sub> is released by a mortar made with getter compared to a mortar made  
10 with  $\gamma$ -MnO<sub>2</sub>, the corresponding value of  $TE_{relative \text{ to } MnO_2}$  is 100%.

11

### 12 3 Results and discussion

13 Firstly, potential interactions between Portland cement paste and  $\gamma$ -MnO<sub>2</sub> or  $\gamma$ -MnO<sub>2</sub>/Ag<sub>2</sub>O  
14 getter are investigated using XRD, TGA and MAS NMR for the cement solids (i.e. the Calcium  
15 Aluminate and Silicate Hydrates C-A-S-H). For the getter itself, SEM/EDS analysis are  
16 performed on powder grains embedded in hardened mortar. The aim is to analyze what  
17 interactions exist between Portland cement paste and  $\gamma$ -MnO<sub>2</sub> or  $\gamma$ -MnO<sub>2</sub>/Ag<sub>2</sub>O.

18 Secondly, gamma Ray irradiation test results are presented and discussed. The hydrogen  
19 trapping efficiency of the mortars added with getter is quantified. The impact of gamma  
20 Rays on the mortar solids and pore structure is investigated by SEM observations and  
21 nitrogen sorption-desorption analysis. The aim is to determine the H<sub>2</sub> trapping efficiency,  
22 and the impact of both hydrogen trapping and gamma Ray irradiation on the mortars.

1

2 **3.1 Interactions between Portland cement pastes and  $\gamma$ -MnO<sub>2</sub> or  $\gamma$ -MnO<sub>2</sub>/Ag<sub>2</sub>O getter**

## 3 3.1.1 XRD results

4 The crystalline phase blend of the powders alone ( $\gamma$ -MnO<sub>2</sub> and getter), and of the Portland  
5 cement pastes at identical W/C=0.5, with or without  $\gamma$ -MnO<sub>2</sub> or getter, is determined by  
6 qualitative XRD (Fig. 3).

7 Fig. 3 shows that  $\gamma$ -MnO<sub>2</sub> and getter powders have very close diffractograms, except for an  
8 additional peak at 33° for getter; both powders are hardly crystalline, so that phase  
9 identification is not straightforward. In particular, the presence of silver carbonate Ag<sub>2</sub>CO<sub>3</sub>,  
10 reputed favorable for trapping [Galliez 2015], is not proven.

11 For the cement pastes, the crystalline phase blend is identical with or without  $\gamma$ -MnO<sub>2</sub> or  
12 getter. It comprises portlandite CH<sup>3</sup>, anhydrous crystals of hatrurite C<sub>3</sub>S, larnite C<sub>2</sub>S and  
13 C<sub>4</sub>AF, ettringite, quartz and mullite (the latter two are present only for Type V cement  
14 paste). Being non-crystalline in commercial Portland cement paste [Lothenbach 2007,  
15 Renaudin 2009], except possibly at the nanometric scale [Zhang 2000], C-A-S-H are hardly  
16 distinguishable in the diffractograms. Similarly, due to slow formation kinetics, calcium  
17 mono-sulfo-aluminate (or AFm for Al<sub>2</sub>O<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub>-mono) is hardly detected after 4 months  
18 curing at ambient temperature (21°C), compared to calcium tri-sulfo-aluminate (i.e. AFt for  
19 Al<sub>2</sub>O<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub>-tri, also ettringite) [Lothenbach 2007].

---

<sup>3</sup> The typical cement notation is used here, where C stands for CaO, H for H<sub>2</sub>O, A for Al<sub>2</sub>O<sub>3</sub>, S for SiO<sub>2</sub> and F for Fe<sub>2</sub>O<sub>3</sub>.

### 1 3.1.2 TGA analysis

2 Table 4 presents mass loss results for cement pastes made with  $\gamma$ -MnO<sub>2</sub> or  $\gamma$ -MnO<sub>2</sub>/Ag<sub>2</sub>O  
3 getter, in the range of (1): 0-105°C, corresponding to the release of physi-sorbed or bound  
4 water (with, in particular, ettringite decomposition), or of (2): 105-400°C, corresponding to  
5 bound water release, i.e. water bound in the C-A-S-H and other more minor phases  
6 [Lothenbach-2007] and of (3): 400-600°C, for portlandite Ca(OH)<sub>2</sub> dehydration. The mass loss  
7 data are corrected for that of  $\gamma$ -MnO<sub>2</sub> or of the getter considered alone. In both cases, with  
8  $\gamma$ -MnO<sub>2</sub> or  $\gamma$ -MnO<sub>2</sub>/Ag<sub>2</sub>O, the free water release is not significantly different, whatever the  
9 cement chosen (Type I or Type V), after the same maturation duration (127 days). The same  
10 conclusion is drawn for bound water and for portlandite amount; there is no significant  
11 difference in presence of  $\gamma$ -MnO<sub>2</sub> or  $\gamma$ -MnO<sub>2</sub>/Ag<sub>2</sub>O.

12 Therefore, from both XRD and TGA, it is concluded that the presence of getter has the same  
13 impact on crystalline cement phases (and water bonding) as  $\gamma$ -MnO<sub>2</sub>. Let now determine  
14 exactly what impact  $\gamma$ -MnO<sub>2</sub> and  $\gamma$ -MnO<sub>2</sub>/Ag<sub>2</sub>O have on C-A-S-H.

### 15 3.1.3 <sup>29</sup>Si MAS NMR results

16 Figure 4 shows the <sup>29</sup>Si spectra (top) and the <sup>27</sup>Al spectra (bottom) for CEM I pastes (at  
17 W/C=0.50 or 0.54, left) and for CEM V pastes (at W/C=0.50 and 0.48, right). Pastes are either  
18 without addition (in blue), or with  $\gamma$ -MnO<sub>2</sub> (in green), or with  $\gamma$ -MnO<sub>2</sub>/Ag<sub>2</sub>O (in purple).

19

#### 20 3.1.3.1- Qualitative analysis of <sup>29</sup>Si spectra

21 Let analyze these spectra first (Fig. 4 top). For both cement types, at - 69 ppm to -74 ppm,  
22 the typical anhydrous phases C<sub>2</sub>S and C<sub>3</sub>S (belite and alite, respectively) provide rather  
23 narrow peaks attributed to Q<sup>0</sup> units [Bruneta 2010]. A slightly smaller amplitude of these

1 peaks is found without addition of  $\gamma$ -MnO<sub>2</sub> or getter, meaning that hydration may be slowed  
2 down by  $\gamma$ -MnO<sub>2</sub> or getter. However, TGA results display no statistically significant difference  
3 between  $\gamma$ -MnO<sub>2</sub> or getter (See Sub-section 3.1.2 and Table 4). It is concluded that  $\gamma$ -MnO<sub>2</sub>  
4 or getter have no significant impact on the hydration of Portland cement paste.

5 Moreover, for both cement types, a typical peak for Q<sup>1</sup>-coordinated Si is located at -79 ppm,  
6 whereas Q<sup>2</sup>(1Al) and Q<sup>2</sup> (i.e. Q<sup>2P</sup> + Q<sup>2b</sup>) resonate at -81 ppm and at -85 ppm respectively.

7 These peaks are attributed to the C-A-S-H [Andersen 2004; Chen 2004; Aono 2007; Girao  
8 2007; Bach 2012; Zhang 2017].

9 For Type I pastes, for all these three peaks, no significant difference in amplitude or peak  
10 position is observed with or without addition. For Type V pastes, for the Q<sup>2</sup>(1Al) and Q<sup>2</sup>  
11 peaks, a slightly smaller amplitude is obtained without addition, but it is not considered  
12 significant with regards to hydration phenomena (see Sub-section 3.1.2). For both Type I and  
13 Type V cements, compared to the reference cement paste, no other peak on the spectra is  
14 observed in presence of  $\gamma$ -MnO<sub>2</sub> or getter. It is concluded that  $\gamma$ -MnO<sub>2</sub> or getter have no  
15 significant impact on the C-A-S-H structure.

16

### 17 3.1.3.2- Quantitative analysis of <sup>29</sup>Si spectra

18 To complete the qualitative analysis, the Q<sup>1</sup> and Q<sup>2</sup> contents, the mean chain length (MCL)  
19 and the (Al/Si) substitution ratio are calculated for each paste and given in Table 5.

20 First, it is observed that for a given cement type, the MCL is remarkably similar whatever the  
21 W/C, with values ranging between 3.3 and 3.7 for Type I Portland cement paste and 6.3 to  
22 7.8 for Type V cement paste.

23 For Type I Portland cement, the MCL values at 7 days are very close to those at 127 days,  
24 with less than 0.8 difference. These MCL values are similar to those determined at an

1 average of 3.3 in [Zhang 2017] for a three-year hydrated paste at W/C=0.43 (made with  
2 super-plasticizer). However, for Type V Portland cement, the MCL increases significantly  
3 from 7 days (with values of 3.6 to 4.4) to 127 days (with values from 6.3 to 7.8, see Table 5),  
4 thanks to hydraulic or pozzolanic reactions with fly ash and blast furnace slag (initially  
5 present in Type V cement). For a similar Type V/A Portland cement paste at W/C=0.39 (with  
6 super-plasticizer), [Zhang 2017] determine a MCL of 21.6 after three years maturation (and  
7 not only 4 months as here).

8 Moreover, the (Al/Si) molar ratios are relatively close for Type I cement pastes, with a mean  
9 value of 0.040 +/-0.012 whatever the W/C and the addition. These are in good agreement  
10 with values found in the literature [Skibsted 1995; Renaudin 2009; Taylor 2010; Pardal  
11 2012]. The (Al/Si) values are significantly higher for Type V cement (with a mean value of  
12 0.139 +/- 0.088 whatever the W/C and the addition), due to an initially greater amount of Al  
13 in the cement anhydrous powder (see Table 1).

14

#### 15 3.1.3.3- Analysis of <sup>27</sup>Al spectra

16 For <sup>27</sup>Al spectra (Fig. 4 bottom), with both cement types, the decomposition provides two  
17 main peaks corresponding to Al(VI) (i.e. aluminum in an octahedric environment), at 10.2-  
18 10.4 ppm (for AFm) and at 13.2-13.4 ppm (for AFt, ettringite). For Type I cement (Fig. 4 left),  
19 two peaks for tetrahedric aluminum environments Al(IV) are attributed to C-A-S-H at 74.0-  
20 74.3 ppm and 70.7-71.2 ppm. A small amplitude peak is at 36.5-37.7 ppm for Al(V)  
21 (pentaedric aluminum, also present in the C-A-S-H). Smaller peaks at 5.2-5.4 ppm, 2.2-  
22 3.1 ppm and (-4.4)-(-2.4) ppm are attributed to aluminum hydrates or hydroxides [Andersen  
23 2006] or to Al(VI) inserted in the C-A-S-H inter-layer space [Mohamed 2020], or even to  
24 hydrotalcite [Nguyen 2018].

1 For Type V cement (Fig. 4 bottom right), apart from AFt and AFm peaks, the second signal  
2 with broader peaks at 73.5-74.1, 67.2-68.3 and 57.2-58.69 ppm are attributed to octahedric  
3 Al(VI) environments due to fly ash, slag and C-A-S-H. The small amplitude peak for Al(V) is  
4 also present at 36.5-37.7 ppm.

5 For both cements, the calculated percentages of AFm, AFt and aluminum hydrates (not  
6 shown, see [Lanier 2020]) are not significantly different without addition, or in presence of  $\gamma$ -  
7 MnO<sub>2</sub> or  $\gamma$ -MnO<sub>2</sub>/Ag<sub>2</sub>O getter.

8  
9 From all these analyses, it is concluded that for both Type I and Type V cement pastes, no  
10 significant difference in their phase assemblage is obtained without any addition or in  
11 presence of  $\gamma$ -MnO<sub>2</sub> or getter, whether regarding the nature of the hydration products or  
12 the progress of cement hydration.

13

### 14 **3.2 SEM observations of the getter embedded in a Portland cement mortar**

15 Let determine whether Ca sorption of the  $\gamma$ -MnO<sub>2</sub>/Ag<sub>2</sub>O getter is actually present in the  
16 mortars designed and manufactured in this research (as in [Pretorius 2001]), by using  
17 SEM/EDS observations.

18 Figure 5(a) is a close-up of a typical MnO<sub>2</sub> grain embedded in epoxy resin, before  
19 incorporation into a mortar. Fig. 5(b) represents the EDS mapping of a getter grain  
20 embedded in a TER-I-54 mortar sample. This shows that the getter grain presents a brim  
21 enriched with Ca, as the pink color (attributed arbitrarily to Ca) highlights. Moreover, a semi-  
22 quantitative EDS analysis is performed over 15 sub-areas of at least 100  $\mu\text{m}^2$  each of the  
23 getter grain surface, where the atoms assumed present are Ca, Mn, C (from the epoxy resin),  
24 O, and Si, yielding 100 %at. An example of an EDS spectrum obtained by this method is

1 provided in Fig. 5(c). It indicates the presence of Ca, calculated from the EDS spectra with an  
2 average percentage on the order of 2.2 to 3.2 %at +/-0.5, depending on the sub-area  
3 considered over the getter grain surface. The EDS analysis also demonstrates (although to a  
4 lesser extent) the presence of Si inside the  $\gamma$ -MnO<sub>2</sub> grains, with a percentage of 1.2 %at +/-  
5 0.5. Neither Ca nor Si were present before incorporation of  $\gamma$ -MnO<sub>2</sub> in the mortar (Fig.5(a)).  
6 The presence of both atoms in the core of a getter grain might imply a limitation in the  
7 trapping efficiency of the getter. Let determine their impact through gamma ray irradiation  
8 tests.

9

### 10 **3.3 Hydrogen trapping efficiency of the Portland cement-based mortars**

11 Gamma ray irradiation tests provide *in situ* hydrogen gas from water radiolysis mechanisms.  
12 Hydrogen is either trapped, or not, inside the getter-added mortars, depending on the  
13 efficiency of the  $\gamma$ -MnO<sub>2</sub>/Ag<sub>2</sub>O getter.  $\gamma$ -MnO<sub>2</sub> powder is incorporated in reference mortars  
14 of identical formulation, as a non-trapping powder.

15 In the following, raw results are presented, normalized and analyzed against the existing  
16 literature on Portland cement-based materials. Secondly, the effect of gamma ray irradiation  
17 on the pore and solid structure of each mortar is investigated, in order to determine  
18 whether they are significantly affected, i.e. whether their durability may be impacted.

#### 19 **3.3.1 Gas production after gamma ray irradiation**

20 Figure 6 displays the nitrogen and hydrogen gas volumes produced by the  $\gamma$ -MnO<sub>2</sub>-based  
21 mortars (Fig. 6(a)) and the getter-based mortars (Fig. 6(b)), depending on the cumulated  
22 dose. In all cases, no gas other than H<sub>2</sub> and N<sub>2</sub> are detected by gas micro-chromatography;



1 CH<sub>4</sub>, O<sub>2</sub>, CO<sub>2</sub> are recorded at zero values. In particular, the absence of O<sub>2</sub> and CO<sub>2</sub> means that  
2 the vial sealing has been efficient (no contact with ambient air).

3 It is also observed that for all samples, either made with  $\gamma$ -MnO<sub>2</sub> or with  $\gamma$ -MnO<sub>2</sub>/Ag<sub>2</sub>O, the  
4 nitrogen production ranges between 0 and 0.5% of the gas volume available in the vial air  
5 space, i.e. it is very limited. Nitrogen may originate from the degradation, due to gamma  
6 rays, of the milling agent present in the Portland cement powder (its exact composition is  
7 unknown).

8 The main interesting comparison is for the hydrogen produced either by  $\gamma$ -MnO<sub>2</sub>-based  
9 mortars or by getter-based mortars. For  $\gamma$ -MnO<sub>2</sub>-based mortars, hydrogen represents  
10 around 2% of the vial air space (at 491 kGy cumulated dose), and twice that value, 4%, for  
11 about twice that cumulated dose (997.5 kGy). On the opposite, for getter-based mortars, the  
12 hydrogen production is only on the order of 0.1-0.2% of the vial air space (at 491 kGy), and  
13 0.2-0.7% at 997.5 kGy. In such case, the hydrogen production is so small that the difference  
14 between the two cumulated doses is not statistically significant.

### 15 3.3.2 Hydrogen production – comparison with the literature

#### 16 3.3.2.1- Trapped gas volume

17 In patent [Lambertin-2010], the H<sub>2</sub> trapping ability is assessed for a Portland cement paste  
18 (at W/C = 0.6) including 30 %wt  $\gamma$ -MnO<sub>2</sub>/Ag<sub>2</sub>O getter, subjected to a 32°C cure for 14 days,  
19 followed by a 60°C heat-treatment for 48h. The measurement includes an external H<sub>2</sub>  
20 source, which is progressively trapped by the getter mixed into the dried cement paste. The  
21 H<sub>2</sub> trapping ability of this paste is of 120 cm<sup>3</sup>/g getter after 40 days in contact with H<sub>2</sub>.

22 In the experiment performed here, Fig. 7 shows that the amount of H<sub>2</sub> trapped by each  
23 mortar ranges between 0.605-0.761 cm<sup>3</sup>/g getter (at 491.2 kGy cumulated dose), and 1.199-

1 1.321 cm<sup>3</sup>/g getter (for the TER-V-48 mortar). On the whole, when doubling the cumulated  
2 irradiation dose (from 491.2 to 997.5 kGy), the trapped H<sub>2</sub> volume by the Portland cement-  
3 based mortars is almost doubled (it ranges from 1.73 to 1.98 times that at 491.2 kGy).  
4 However, the recorded values are significantly smaller than for the cement paste in  
5 [Lambertin-2010]. Indeed, in our experiment, H<sub>2</sub> is generated by water radiolysis in smaller  
6 amounts than what is available from an external H<sub>2</sub> source (as in [Lambertin-2010]).  
7 Moreover, in our research, no preliminary drying of the mortars (which favors trapping) is  
8 performed.

9

#### 10 3.3.2.2- Hydrogen radiolytic yield

11 Fig. 8 shows the normalized hydrogen radiolytic yield  $\frac{G(H_2)_{material}}{w_{water}}$  of all the mortar samples

12 made with  $\gamma$ -MnO<sub>2</sub> or  $\gamma$ -MnO<sub>2</sub>/Ag<sub>2</sub>O getter, compared to that of pure water.

13 Mortars made with  $\gamma$ -MnO<sub>2</sub> have significant hydrogen production rates, with values ranging  
14 between 3.42 and 6.87 x10<sup>-8</sup> mol/J, depending on the mortar and on the sample considered.

15 For all samples (except for one TER-V-48, which may have leaked during the measurement  
16 process), this is consistently greater than the value for pure water (4.46 x 10<sup>-8</sup> mol/J). These

17 yield values are compared to usual ones for Portland-cement based materials from the  
18 literature (see below). The smallest radiolytic yield is obtained with TER-I-54, although TER-  
19 V-48 and QUAT-V-48 are close.

20 For mortars made with  $\gamma$ -MnO<sub>2</sub>/Ag<sub>2</sub>O, the hydrogen production is significantly smaller, with  
21 values of 0.185 to 1.13 x10<sup>-8</sup> mol/J, again depending on the mortar and on the sample  
22 considered. Although the difference is very limited, the QUAT-V-48 mortar traps the greatest  
23 amount of H<sub>2</sub> (i.e. it releases the smallest amount of H<sub>2</sub>), and the TER-V-48 mortar traps the  
24 smallest amount.

1 Complementarily, Fig. 9 compares the normalized radiolytic yield  $\frac{G(H_2)_{material}}{w_{water}}$  of the  
2 designed mortars to that of pure water, and to those found in the literature for Portland-  
3 based cement pastes of various compositions, depending on their mass water content  
4  $w_{water}$  [Möckel 1982; Chartier 2017; Acher 2018].

5 As in Fig. 8, it is observed that the mortars made with  $\gamma$ -MnO<sub>2</sub> have a greater radiolytic yield  
6 than pure water (between 5.35-6.87 x10<sup>-8</sup> mol/J without the TER-V-48 outlier, compared to  
7 4.46 x 10<sup>-8</sup> mol/J for pure water). Former studies have quantified the same tendency as in  
8 our research, but for Portland cement pastes, although these are made without  $\gamma$ -MnO<sub>2</sub>. In  
9 particular, for a white Portland cement paste with a mass water content  $w_{water}$  of 0.35,  
10 [Chartier 2017] measure a radiolytic yield of 4.72 x 10<sup>-8</sup> mol/J; greater values (up to 6 x 10<sup>-8</sup>  
11 mol/J) are obtained for smaller  $w_{water}$ . In [Möckel 1982], measured values for the radiolytic  
12 yield are above 8 x 10<sup>-8</sup> mol/J, for  $w_{water}$  of 0.32-0.35. Although [Acher 2018] measures  
13 smaller yields than pure water, most of the values in [Möckel 1982; Chartier 2017] are above  
14 the radiolytic yield of pure water.

15

### 16 3.3.2.3- Understanding the radiolytic yield of Portland cement-based mortars

17 An explanation for the greater H<sub>2</sub> radiolytic yield of Portland cement pastes compared to  
18 pure water is given in [Chupin 2017; Yin 2019; Cantarel 2020]. A significant linear energy  
19 transfer (LET) from the cement paste solids to the liquids is inferred.

20 Indeed, in a Portland cement mortar, water is not homogeneously distributed; it is  
21 integrated in the heterogeneous medium that is the cement paste (made of remains of  
22 anhydrous cement, of C-A-S-H, CH, etc.), and also in the ITZ (Interfacial Transition Zone)  
23 [Larbi 1993; Scrivener 2004], which is present between paste and aggregates. In cement  
24 paste pores smaller than 15 nm, G. Scherer and co-workers [Valenza 2005; Xu 2009a; Xu

1 2009b] have shown experimentally that water is confined, with limited mobility and  
2 anomalously high thermal expansion properties.

3 More directly, [Yin 2019] have subjected synthetic C-A-S-H (i.e. the main component of a  
4 Portland cement paste) to gamma rays on the same Gammatec installation as in this  
5 research. The molar calcium-to-silicium (C/S) ratio of the C-A-S-H ranges from 0.8 to 1.4, and  
6 aluminum is absent, so that the experiment is rather on C-S-H than C-A-S-H. For all C-S-H, the  
7 normalized radiolytic yield is greater than that of pure water. The authors relate the  
8 radiolytic yield to the C/S ratio, to the C-S-H interlayer space, and also to the surface specific  
9 area (SSA) of the C-S-H. In the C-S-H, the interlayer space corresponds to pores of 0.9 to 1.4  
10 nm where a so-called crystallization water is located; due to the small pore sizes involved,  
11 this water is considered located in a confined environment, i.e. in locations where water  
12 radiolysis (among other phenomena [Valenza 2005; Xu 2009a; Xu 2009b]) may be strongly  
13 affected.

14 Experimentally, [Yin 2019] show that the greater the interlayer space (and the SSA), the  
15 greater the radiolytic yield, and the smaller the C/S ratio of the C-S-H. Whenever the C/S is  
16 smaller, a smaller proportion of Ca compared to Si is present in the C-S-H, meaning that a  
17 longer silicate chain of the C-S-H is involved [Haas 2012]. In other words, a greater radiolytic  
18 yield is associated to a longer dreierketten-type silicate chain of the C-S-H [Geng 2017], to a  
19 greater interlayer space and to a greater SSA, and the energy transfer (due to irradiation) is  
20 greater from the C-A-S-H solids to confined water than in free water.

21 This is also expressed by [Chupin 2017] when stating that the greater the SSA of a porous  
22 medium is, the greater its radiolytic yield is. Indeed, when a significant surface allowing  
23 exchanges between solids/liquid exists, the energy transfer events (originating from the  
24 gamma rays) are more numerous than in free water.

1 Let relate this analysis to the mortars tested in this research. Table 6 provides the SSA of all  
2 mortars (made with  $\gamma$ -MnO<sub>2</sub> or  $\gamma$ -MnO<sub>2</sub>/Ag<sub>2</sub>O getter) measured by the BET approach, before  
3 and after irradiation and at the same age. For all mortars before irradiation, the SSA ranges  
4 between 5.4-5.5 m<sup>2</sup>/g (for QUAT-V-48), 6.0-6.9 m<sup>2</sup>/g (for TER-V-48) and 9.2-10.2 m<sup>2</sup>/g (for  
5 TER-I-54). These values represent half the SSA of the cement paste of the [Lambertin 2010]  
6 patent (the latter has a SSA of 21.9 m<sup>2</sup>/g). After irradiation, the SSA of all mortars is  
7 consistently lower than before irradiation, with values ranging between 3.5-4.1 m<sup>2</sup>/g (for  
8 QUAT-V-48), 3.8-4.2 m<sup>2</sup>/g (for TER-V-48) and 4.1-6.1 m<sup>2</sup>/g (for TER-I-54). The TER-I-54 mortar  
9 has the greatest SSA before and after irradiation.

10 The results mean that irradiation significantly reduces the SSA of all mortars, possibly due to  
11 enhanced energy transfer events (inside confined spaces present in the C-S-H). As a matter  
12 of comparison, the mass loss after irradiation is very limited, of around 0.06-0.56 % (Table  
13 6). The decrease in SSA is more pronounced for mortars made with getter than for those  
14 made with  $\gamma$ -MnO<sub>2</sub>. As discussed above, changes in the SSA are attributed to intense energy  
15 transfer from the solids to the liquid (i.e. to the porewater).

16 In order to further ascertain this, it would be interesting to compare these results to the  
17 same mortars made with a simulant of  $\gamma$ -MnO<sub>2</sub>, e.g. with a fine inert filler powder.

### 18 3.3.3 Hydrogen trapping efficiency

19 Fig. 10 summarizes the trapping efficiency (TE) of all three mortars after 491.2 or 997.5 kGy  
20 gamma irradiation. TE is expressed either relatively to pure (free) water (Fig. 10(a)) or  
21 relatively to the same mortar made with MnO<sub>2</sub> (Fig. 10(b)).

22 In both cases, the trapping efficiency is of 85-92% for TER-I-54 mortar, 77-92% for TER-V-48  
23 and 93.9-96.4% for QUAT-V-48 mortar. In other words, at least 77% (and as much as 96.4%)

1 of the hydrogen produced in the absence of getter is trapped when it is incorporated in the  
2 mortar formulation. The mortar with the best trapping performance is the QUAT-V-48,  
3 which requires the preliminary manufacturing of getter granules (out of the three mortars, it  
4 is the most expensive to manufacture at an industrial scale). However, it is concluded that all  
5 three mortars have an excellent trapping ability for hydrogen gas at both gamma irradiation  
6 doses.

### 7 3.3.4 Changes in mortar microstructure after gamma ray irradiation

8 Apart from changes in the SSA, this last part investigates whether other changes in mortar  
9 microstructures are observed after irradiation up to 997.5 kGy cumulated dose, which may  
10 affect their durability.

#### 11 3.3.4.1 Solid structure

12 Fig. 11(a) shows general views of a typical mortar microstructure (at a low magnification of  
13 x300), on the example of TER-I-54, made with  $\gamma\text{-MnO}_2/\text{Ag}_2\text{O}$  getter. The polished sample  
14 surface is observed with the BSE detector, i.e. with grey levels representative of the atomic  
15 number of the atoms present; the whiter grains are  $\gamma\text{-MnO}_2/\text{Ag}_2\text{O}$ , the large darker grey  
16 areas are silica sand grains, the black areas are pores and the rest is cement paste. For TER-I-  
17 54, a good spatial homogeneity of the  $\gamma\text{-MnO}_2$  grains is visible on both images (Fig. 11(a)).  
18 Similar results are obtained with  $\gamma\text{-MnO}_2$  and for the two other TER-V-48 and QUAT-V-48  
19 mortars.

20 Comparatively, Fig. 11 (b) shows the structure of the same TER-I-54 mortar after irradiation,  
21 at a close magnification (x220) to that in Fig. 11(a). At that scale, no significant difference is  
22 observed with the same mortar before irradiation (Fig. 11(a)). In particular, no specific  
23 cracking is present (other than a very limited cracking pattern – seen there before

1 irradiation, and which is usual for SEM vacuumed samples). No other difference is noted  
2 when using higher magnifications, up to x10k. It is concluded that the irradiation performed  
3 does not change the general mortar structure as observed by SEM.

#### 4 3.3.4.2 Pore structure

5 Following porosity before irradiation (see Appendix A.1) and SSA measurements (see sub-  
6 section 3.4.2), the pore network of the mortars has been investigated in more detail through  
7 pore size distributions (PSD) (Fig. 12). With nitrogen sorption-desorption, the same mortar  
8 formulation is tested with  $\gamma$ -MnO<sub>2</sub> or with  $\gamma$ -MnO<sub>2</sub>/Ag<sub>2</sub>O getter, before and after irradiation.  
9 Whatever the mortar considered, pore sizes measured by nitrogen sorption-desorption  
10 range from 2-3 nm to about 150 nm. Bimodal PSD are obtained, as expected from the  
11 literature for Portland cement-based materials [McDonald 2010; Scrivener 2011; Yio 2014].  
12 For instance, for TER-I-54 made with  $\gamma$ -MnO<sub>2</sub> (Fig. 12(a)), the main peak pore size is of 54 +/-  
13 2 nm (corresponding to pores located between C-A-S-H gel clusters [McDonald 2010;  
14 Scrivener 2011; Yio 2014]), and the secondary peak is at 3.4 nm (corresponding to C-A-S-H  
15 inner-cluster pores [McDonald 2010; Scrivener 2011; Yio 2014]). The main peak pore size is  
16 slightly smaller for TER-V-48 (respectively for QUAT-V-48) made with  $\gamma$ -MnO<sub>2</sub>, with a value  
17 53 nm (resp. 50 nm). The secondary peak is at an identical value.

18 Moreover, whether the mortar is made with  $\gamma$ -MnO<sub>2</sub> or with  $\gamma$ -MnO<sub>2</sub>/Ag<sub>2</sub>O getter, no  
19 significant difference in peak pore sizes is observed. After 1 MGy gamma irradiation, no  
20 significant difference in peak pore sizes is observed either, for the mortars made with  $\gamma$ -  
21 MnO<sub>2</sub> or with  $\gamma$ -MnO<sub>2</sub>/Ag<sub>2</sub>O getter.

22 However, for all mortars, the amplitude of the peaks is generally smaller after irradiation.

23 This means that irradiation does not affect the pore size distributions of the trapping

1 mortars, but it induces a decrease in the differential pore volume; less pore volume is  
2 available after irradiation. This is consistent with the decrease in the SSA measured after  
3 irradiation (Table 6). Both observations are attributed to intense energy transfer from the  
4 solids to the liquid (i.e. to the porewater), particularly in nanometric sized pores.

## 5 4 Conclusions

6 This research has assessed the structure changes and the hydrogen trapping efficiency of  
7 three novel formulations of Portland cement-based mortars, TER-I-54, TER-V-48 and QUAT-  
8 V-48, incorporating a  $\gamma$ -MnO<sub>2</sub>/Ag<sub>2</sub>O getter, for improving the safety of radioactive waste  
9 storage.

- 10 • By using XRD, TGA and MAS NMR of <sup>29</sup>Si and <sup>27</sup>Al nuclei, it is shown that the structure of  
11 the Portland cement solids (i.e. the C-A-S-H) is not impacted by the presence of getter,  
12 even after several month curing. Conversely, SEM+EDS analysis shows that calcium Ca  
13 and Si (initially in the cement porewater) are present at the surface and in the core of the  
14  $\gamma$ -MnO<sub>2</sub>/Ag<sub>2</sub>O getter grains, and may reduce its trapping ability.
- 15 • After gamma irradiation, all three mortars made with  $\gamma$ -MnO<sub>2</sub> or getter powder release  
16 more hydrogen gas than pure water subjected to the same integrated dose. This is  
17 consistent with the literature on Portland-cement pastes, which clearly demonstrates  
18 their greater hydrogen production compared to pure water, due to extensive energy  
19 transfers between the paste solids (the C-A-S-H) and the water confined in its pores (in  
20 particular those trapped below 15 nm pore diameter).
- 21 • No particular effect of  $\gamma$ -MnO<sub>2</sub>, towards enhancing H<sub>2</sub> production, is identified from  
22 these irradiation experiments alone.



1 • On the opposite, for mortars added with  $\gamma\text{-MnO}_2/\text{Ag}_2\text{O}$  getter, trapping is significant,  
2 with an efficiency ranging between 77 and 96.4%, depending on the integrated dose and  
3 formulation considered. This efficiency is measured as the relative amount of  $\text{H}_2$  trapped  
4 by the monolithic mortar, compared to the amount produced with  $\gamma\text{-MnO}_2$  mortars, or to  
5 the amount produced by free water.

6 It is concluded that the developed mortars display excellent hydrogen trapping efficiency,  
7 without any impact on their solid structure. This is favorable to their durability, from a  
8 geochemistry viewpoint.

9

10 In further research, the efficiency of  $\text{H}_2$  mitigation should be tested with much higher  
11 gamma doses ( $>10$  MGy) to assess the robustness of the Portland cement-based mortar  
12 solutions. This has been published only for reference cementitious pastes (without getter or  
13  $\text{MnO}_2$ ) in [Varlakov 2021].

14 Besides, it would be useful to assess the properties and the trapping efficiency of the novel  
15 cement matrices at later ages, in drier conditions (i.e. at lower  $S_w$ ), in varied aggressive  
16 environments (e.g. due to accelerated carbonation or in presence of chemically aggressive  
17 liquids), and after accidental scenarii (such as after a fire). Extending the research to actual  
18 tritium trapping would also be useful for industrial applications, e.g. for the immobilization  
19 of ITER tritiated waste.

20 Finally, considering tritium concern, the proposed getter can reduce  $\text{T}_2$  or HT releases but  
21 cannot prevent tritiated water to be released from the wastefoms in case of drying. This will  
22 also require additional investigation.

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## Appendices

### A.1- Materials (complements)

**A.1.1- Powders.** Cement pastes and mortars are made either with pure Portland cement, of reference CEMI 52.5R CE CP2 NF (Lafarge, Saint Pierre La Cour factory, France), or with composed Portland cement, of reference CEM V/A (S-V) 32.5N-LH HSR LA (CCB Cementir Holding, Gaurain-Ramecroix factory, Belgium).

The  $\gamma$ -MnO<sub>2</sub>/Ag<sub>2</sub>O getter is provided by A3I (France), with typical grain sizes  $d_{10} = 4.5 \mu\text{m}$ ,  $d_{50} = 13.7 \mu\text{m}$  and  $d_{90} = 33.0 \mu\text{m}$  (Fig. 1). Its apparent density is  $3.19 \text{ g/cm}^3$ , derived from the absolute density of MnO<sub>2</sub> ( $5.45 \text{ g/cm}^3$ ) [Green 2018], a total porosity of 84% and a pore volume of  $0.13 \text{ cm}^3/\text{g}$  given by nitrogen sorption-desorption. The particle size distribution (PSD) of MnO<sub>2</sub> powder is characterized by  $d_{10} = 3.2 \mu\text{m}$ ;  $d_{50} = 9.8 \mu\text{m}$ ;  $d_{90} = 18.0 \mu\text{m}$ .

Both  $\gamma$ -MnO<sub>2</sub> and  $\gamma$ -MnO<sub>2</sub>/Ag<sub>2</sub>O powders have PSD similar to Type I cement ( $d_{10} = 4.4 \mu\text{m}$ ,  $d_{50} = 13.0 \mu\text{m}$  and  $d_{90} = 26.3 \mu\text{m}$ ) and Type V cement ( $d_{10} = 4.1 \mu\text{m}$ ,  $d_{50} = 12.7 \mu\text{m}$  and  $d_{90} = 46.6 \mu\text{m}$ ). However, their specific surface area, measured by the BET method (Table 1) is one order of magnitude greater. Their chemical composition is also given in Table 1. It shows the high purity of  $\gamma$ -MnO<sub>2</sub> and  $\gamma$ -MnO<sub>2</sub>/Ag<sub>2</sub>O powders. X-ray diffraction results of  $\gamma$ -MnO<sub>2</sub> and  $\gamma$ -MnO<sub>2</sub>/Ag<sub>2</sub>O powders indicate that both powders are poorly crystalline (see [Lanier 2020]).

**A.1.2- Sand.** For mortar manufacturing, a pure silica sand (SNL, Leucate, France) is used, with a standard particle size distribution (according to European standard EN196-1) characterized by sieving with  $d_{10} = 0.15 \text{ mm}$ ,  $d_{50} = 0.63 \text{ mm}$  and  $d_{90} = 1.25 \text{ mm}$ . Its main grain size classes are described in EN196-1, as 0.63-1.25 mm (it is the most important class in mass proportion, at 36%wt +/-1), 1.25-2.50 mm (second in mass proportion, at 20%wt +/-1),

1 0.315-0.63 mm (third in mass proportion, at 17%wt +/-2), 0.16-0.315 mm (fourth in mass  
2 proportion, at 14%wt +/-1), and 0.08-0.16 mm (fifth in mass proportion, at 13% +/-1); sand  
3 grains in the range 0.063-0.08 mm are neglected because they represent less than 1%wt.

4 **A.1.3- Super-plasticizer.** All mortars are made with a proportion of Master Glenium 27  
5 (BASF, France) super-plasticizer, corresponding to 2%wt cement. It is a non-chlorinated  
6 additive based on modified polycarboxylic ethers, chosen for its compatibility with ionizing  
7 rays emitted by the waste [Kotatkova 2018].

8 **A.1.4- Reference paste material.** The Portland cement paste described in [Lambertin 2010],  
9 labelled PASTE-REF-CEMI, is made with pure Type I Portland cement, water to a cement  
10 mass ratio W/C of 0.6, and 30 %wt getter (Table 2). After mixing, the paste is sealed in a  
11 hermetic container, cured for 14 days in an oven at 32 °C, then unsealed and oven-dried at  
12 60 °C for 48 hours. For this paste, drying at 60°C is considered essential to drain the pore  
13 network and allow gas transport.

14 Let analyze here the porosity differences with the trapping mortars developed herein. After  
15 60°C drying, the porosity of all three trapping mortars is very similar, with values ranging  
16 between 15.2 % +/-0.4 and 17.1 % +/-0.6 (Table 6). These are less than half the porosity of  
17 PASTE-REF-CEMI. Given that without drying, this porosity is also partially filled with water, all  
18 trapping mortars are bound to have a much more limited gas transport ability than PASTE-  
19 REF-CEMI. This is assumed favorable to let H<sub>2</sub> gas more time to flow through and be trapped  
20 by the getter present inside the mortars.

21 **A.1.5- Paste manufacturing, curing and drying.** Each paste is made with the same cement  
22 mass (15g). For pastes containing  $\gamma$ -MnO<sub>2</sub> or  $\gamma$ -MnO<sub>2</sub>/Ag<sub>2</sub>O powder, the latter is added  
23 during mixing (with a mechanical stirrer at 140 rpm) as a supplement to the paste, and

1 represents 10% of the total paste mass. For instance, the Type I Portland cement paste at  
2 W/C=0.48 is made with 15,00 g cement, 7,20 g deionized water and 2,46 g  $\gamma$ -MnO<sub>2</sub> or getter.  
3 Each paste is cured in an airtight container i.e. in endogenous conditions at a constant  
4 temperature of 21°C for 127 days (4 months), in order to ensure sufficient maturation.  
5 Nota: Other samples have also been tested after 7 days curing. They provide similar results  
6 to those at 127 days (see [Lanier 2020]). With MAS NMR, anhydrous CEM I and CEM V  
7 cement powder samples are also tested in the same conditions for comparison purposes.

## 8 **A.2- Classical characterization methods**

9 **A.2.1- Mortar pore structure.** For non-irradiated materials, the mortars are matured for 4  
10 months, and oven-dried at 100°C until mass stabilization. The pore structure is quantified up  
11 to a size of about 200 nm with nitrogen sorption-desorption isotherms, obtained with a  
12 Micromeritics ASAP 2020 device, and up to a size of 1 mm with a Micromeritics Autopore IV  
13 9500 Mercury Intrusion Porosimeter (MIP). Pore Size Distributions (PSD) are deduced from  
14 desorption curves, for pores bigger than 3 nm, using the Barrett-Joyner-Halenda (BJH) model  
15 [Rouquerol 2014]. As a matter of comparison, nitrogen experiments are also conducted for  
16 the  $\gamma$ -MnO<sub>2</sub> and  $\gamma$ -MnO<sub>2</sub>/Ag<sub>2</sub>O powders.

17 After irradiation, mortar samples are retrieved, dried at 100°C until mass stabilization, and  
18 tested for nitrogen sorption-desorption isotherms with the same procedure as non-  
19 irradiated material (Table 6).

20 Using sample dry mass  $m_{dry}$ , sample porosity  $\phi$  is measured as:

$$21 \quad \phi = \frac{V_{voids\ total}}{V_{sample}} = \frac{(m_{ethanol\ saturated} - m_{dry})}{\rho_{ethanol} V_{sample}}$$

22 Where  $V_{voids}$  is the voids volume,  $V_{sample}$  is sample volume (measured with a caliper to an  
23 accuracy of 0.1 mm),  $m_{ethanol\ saturated}$  is the ethanol saturated mass of the sample, and

1  $\rho_{ethanol}$  is ethanol volumetric mass (taken at a value of 789 kg/m<sup>3</sup> at 20°C). For sample  
2 saturation, ethanol is preferred to water or oil, because it does not significantly react with  
3 Portland cement [Zhang 2011], and its viscosity is sufficiently low to allow sample saturation.

4

5 **A.2.2- SEM observations of mortars.** After 4 months endogenous curing, each mortar  
6 sample for SEM analysis is oven-dried at 100°C until mass stabilization. Following that, each  
7 sample is impregnated with epoxy resin (Epofix, Struers), polished until mirror surface finish  
8 and coated with 20nm thick carbon. The SEM is a JEOL JSM-7800F LV with a FEG source,  
9 equipped with secondary and backscattered electron detectors (SE and BSE) and coupled to  
10 an Energy Dispersive Spectroscopy (EDS) detector, operated with the Aztec Oxford  
11 Instruments software. The accelerating voltage is kept constant at 15kV and the working  
12 distance at a constant value of 10 mm +/-0.1. For qualitative EDS analysis, the dead time is  
13 kept at 30%+/-5 throughout.

14

15 **A.2.3- TGA analysis of cement pastes.** Thermogravimetry is performed from room  
16 temperature to a target temperature of 1100°C, at a slow heating rate of 5°C per minute,  
17 under an argon atmosphere. The device used is a SETARAM© thermal analyzer TG-92.  
18 Preliminarily to testing the powdered cement pastes, the  $\gamma$ -MnO<sub>2</sub> and the getter powders  
19 alone are tested. Their mass loss is deduced from that of the corresponding paste at the  
20 same temperature.

21 The portlandite mass percentage is calculated from the mass loss in the temperature range  
22 from 400 to 600°C [Mounanga 2003] [Stephant 2015] as:

1                      Portlandite mass % =  $\frac{\Delta m_{corrected}(400 - 600^{\circ}C)}{m_{initial\ sample}} * \frac{M(Ca(OH)_2)}{M(H_2O)}$

2                      Where  $\Delta m_{corrected}(400 - 600^{\circ}C)$  is the sample mass variation between 400 and 600°C,  
3                      corrected for that of the MnO<sub>2</sub> (or getter) alone,  $m_{initial\ sample}$  is the sample initial mass,  
4                       $M(Ca(OH)_2)$  is portlandite molar mass and  $M(H_2O)$  is water molar mass.

5

### 6                      **A.3 Experimental protocol for gamma irradiation measurements**

7                      After at least one week endogenous curing, each sample is removed from its mold and  
8                      placed in a sealed glass container without any further conditioning (i.e. no drying or water  
9                      saturation). This means that all samples are monoliths, and not crushed or powdered  
10                     mortars. The industrial irradiator uses a gamma ray <sup>60</sup>Co source, in the Gammatec facility at  
11                     CEA Marcoule (Fig. 2 left).

12                     In order to quantify the released H<sub>2</sub> amounts, a waiting time of about 1.5 months (i.e. 38-42  
13                     days) is observed before analyzing the atmosphere of the glass container, i.e. of the gaseous  
14                     sky in the glass vials, by micro-gas chromatography (micro-GC), with an accuracy down to  
15                     micro-mol of gas, see Fig. 2 right. This waiting time corresponds to the time necessary for H<sub>2</sub>  
16                     to flow out of the mortar monoliths by diffusion phenomena. Gas diffusion and permeability  
17                     are related phenomena in cement-based materials, in the sense that they both highly  
18                     depend on water saturation level S<sub>w</sub> [Sercombe 2007].

19                     Following the experiment, the amount of gas (H<sub>2</sub> but also O<sub>2</sub>, CH<sub>4</sub> or N<sub>2</sub>) released by the  
20                     samples  $n(gas)$  is calculated (in mol) using the perfect gas law, from the raw gas volume  
21                     percentage %*vol* directly provided by micro-GC, from the gas pressure  $P_f$  (in Pa) in the vial  
22                     after irradiation and from the free vial volume  $V_{free}$  (expressed in m<sup>3</sup>), as [Lanier 2020]:

1 
$$n(gas) = \frac{P_f \times \%vol \times V_{free}}{R \times T}$$

2 with R perfect gas constant (in J.mol<sup>-1</sup>.K<sup>-1</sup>) and T sample temperature in K<sup>-1</sup>.

3 The gas radiolytic yield of the considered mortar (in mol/J) is then calculated as in [Chartier  
4 2017] by:

5 
$$G(gas)_{material} = \frac{n(gas)}{D m}$$

6 where  $n(gas)$  is in mol, D is the cumulated dose in Gy, and m is the total sample mass (in  
7 kg).

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1 **Tables**

2

Oxide \ mass %	Type I (CEMI) cement	Type V (CEMV) cement	$\gamma$ -MnO <sub>2</sub>	$\gamma$ -MnO <sub>2</sub> /Ag <sub>2</sub> O getter
CaO	63.88	48.24	0	0
SiO <sub>2</sub>	17.26	25.59	0	0
SO <sub>3</sub>	5.14	5.75	0.63	0
Al <sub>2</sub> O <sub>3</sub>	3.72	8.77	0	0
Na <sub>2</sub> O	3.00	0	0	0
Fe <sub>2</sub> O <sub>3</sub>	2.79	3.13	0	0
MgO	1.90	5.20	0	0
K <sub>2</sub> O	1.61	2.29	0	0
TiO <sub>2</sub>	0.17	0.57	0	0
MnO <sub>2</sub>	0.1	0.1	98.90	85.01
Ag <sub>2</sub> O	0	0	0	14.97
BaO	0	0	0.32	0
SrO	0	0	0.07	0
S <sub>BET</sub> (m <sup>2</sup> /g)	2.36	2.22	77.93-80.2	57.5-59.5
S <sub>BJH</sub> (m <sup>2</sup> /g)	2.45	2.19	86.6-87.7	67.8-69.8
BJH desorption average pore diameter (nm)	N/A	N/A	6.22-6.25	6.16-6.18
Minimum-Maximum pore diameters measured by nitrogen sorption-desorption (nm)	N/A	N/A	[1.8; 141.6 +/- 4.4]	[1.7; 129 +/- 2.5]

3

4 Table 1: X ray fluorescence results, specific surface area (measured by the BET or by the BJH  
5 approach) and pore size distribution (also measured by nitrogen sorption-desorption) for the  
6 powders involved in this research.

7

Material name	PASTE-REF-CEMI	TER-I 54	TER-V 48	QUAT-V 48
Cement type	Type I	Type I	Type V	Type V
W/C	0.6	0.54	0.48	0.48
Water (g)	262.5	243	216	216
Cement (g)	437.5	450	450	450
$\gamma$ -MnO <sub>2</sub> powder (g)	300	202.5	202.5	162
$\gamma$ -MnO <sub>2</sub> granules (g)	-	-	-	68 g, comprising 40.5 g MnO <sub>2</sub> , 15.5 g cement and 12 g water
$\gamma$ -MnO <sub>2</sub> (% total mortar volume)	6.3	6.8	7.0	7.1
Silica sand class (1.25mm <d≤ 2.5mm) (g)	-	945	945	877
Silica sand class (0.063mm <d≤ 0.160mm) (g)	-	202.5	202.5	243
Super-plasticizer (g)	-	9	9	9
Corresponding volume (L)	0.50	0.90	0.90	0.90
Apparent density (g/cm <sup>3</sup> )	2.00	2.28	2.25	2.17
Total water volume (%total vol)	52.5	27	24	24
Average ASTM spread (cm)	4.5 (slump)	20.5	22.3	21.3
Vicat setting duration (and start)	N/A	7h15 (starts after 4h mixing)	9h30 (starts after 6h30 mixing)	9h (starts after 4h30 mixing)

1

2 Table 2: Formulations of the novel Portland-based mortars (named TER-I-54, TER-V-48 and  
3 QUAT-V-48) designed to best comply with the industrial specifications, and their fresh state  
4 properties.

Mortar name (either made with $\gamma$ -MnO <sub>2</sub> or with $\gamma$ - MnO <sub>2</sub> /Ag <sub>2</sub> O getter)	Portland cement type	Maturation duration at irradiation (days)	Cumulated dose (kGy)	Duration of the irradiation tests (days)	Duration between irradiation and $\mu$ GC (days)	Cumulated age at measurement (days)
TER-I 54	Pure (Type I)	118	491.2 or 997.5	23 or 46	39	157
TER-V 48	Composed (Type V)	117	491.2 or 997.5	23 or 46	38	155
QUAT-V 48	Composed (Type V)	115	491.2 or 997.5	23 or 46	42	157

1

2 Table 3: Main characteristics of the gamma ray irradiation tests: mortar type, mortar age at

3 gamma irradiation, cumulated dose sustained (2 samples per dose), duration of the

4 irradiation tests, waiting time between irradiation and micro-Gas Chromatography ( $\mu$ GC),

5 and cumulated age at gas production measurement.

6



1

Cement paste name	Maturation duration (days)	Corrected $\Delta m$ between 0 and 105°C (%)	Corrected $\Delta m$ between 105 and 400°C (%)	Corrected $\Delta m$ between 400 and 600°C (%)	Portlandite mass % (+/-1%)
54-I-MnO <sub>2</sub>	127	5.9	11.4	4.8	19.9
54-I-G	127	6.6	10.4	4.9	20.3
48-V-MnO <sub>2</sub>	127	6.1	10.4	2.7	11.2
48-V-G	127	4.6	11.5	2.4	10.0

2

3 Table 4: TGA results for Type I cement paste at W/C=0.54 and Type V cement paste at  
4 W/C=0.48 made with either  $\gamma$ -MnO<sub>2</sub> or  $\gamma$ -MnO<sub>2</sub>/Ag<sub>2</sub>O getter (labelled G). Values are given at  
5 +/-1%. Corrected mass variations correspond to mass loss data accounting for the mass loss  
6 of the  $\gamma$ -MnO<sub>2</sub> or getter considered alone.

1  
2

Cement paste name	Anhydrous cement content (%)	Q <sup>1</sup> content (%)	Q <sup>2</sup> content (%)	Mean Chain Length (MCL)	(Al/Si)
<b>50-I-127d</b>	12,8	55,1	32,1	3,3	0,039
<b>50-I-MnO<sub>2</sub>-127d</b>	10,8	54,0	35,2	3,4	0,042
<b>50-I-G-127d</b>	14,5	49,0	36,5	3,7	0,046
<b>54-I-127d</b>	8,5	55,6	35,9	3,4	0,040
<b>54-I-MnO<sub>2</sub>-127d</b>	9,2	55,6	35,2	3,4	0,028
<b>54-I-G-127d</b>	11,0	51,0	38,0	3,6	0,041
<b>50-V-127d</b>	39,4	21,6	39,0	6,4	0,131
<b>50-V-MnO<sub>2</sub>-127d</b>	39,6	21,4	39,0	6,4	0,131
<b>50-V-G-127d</b>	36,0	22,5	41,5	6,4	0,134
<b>48-V-127d</b>	31,8	24,5	43,7	6,3	0,138
<b>48-V-MnO<sub>2</sub>-127d</b>	37,1	18,6	44,3	7,8	0,154
<b>48-V-G-127d</b>	35,5	21,6	42,9	6,8	0,146

3

4 Table 5: Computed <sup>29</sup>Si MAS NMR results providing the anhydrous cement content, the Q<sup>1</sup>  
5 and Q<sup>2</sup> content, the Mean Chain Length (MCL) of the C-A-S-H and the average (Al/Si) molar  
6 ratio of the C-A-S-H (indicative of Al substitutions to Si) for Portland cement pastes made  
7 with W/C=0.50 and 0.54 (Type I cement), or 0.48 and 0.50 (Type V cement), after 127 days  
8 maturation in endogenous conditions. For instance, 50-I stands for W/C=0.50, Type I

9

Portland cement paste with neither  $\gamma$ -MnO<sub>2</sub> nor getter (G).

10

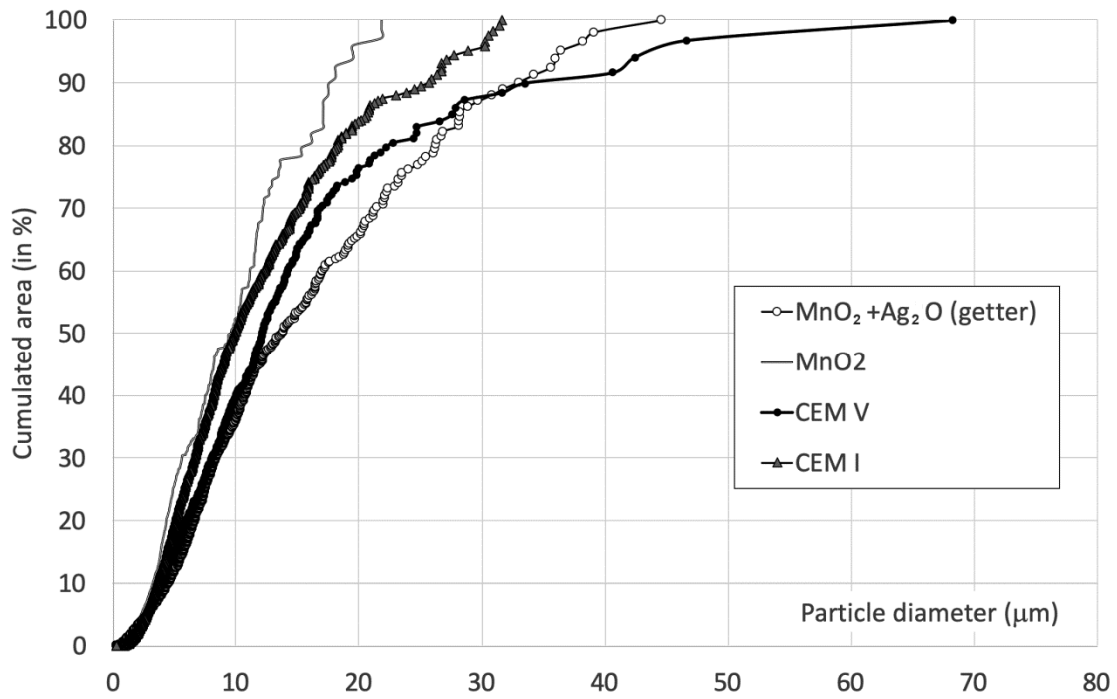
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Material label	MnO <sub>2</sub> or (MnO <sub>2</sub> /Ag <sub>2</sub> O) getter	irradiated or not	BET Specific Surface Area SSA (m <sup>2</sup> /g)	Mass loss after irradiation (% mass before irradiation)	Porosity (%)
PASTE-REF-CEMI	getter	No	21.9	-	37.2 +/- 0.5
TER-I 54-NI	γ-MnO <sub>2</sub>	No	9.16	-	15.2 +/- 0.4
TER-I 54-NI	getter	No	10.17	-	-
TER-I 54-IR	γ-MnO <sub>2</sub>	Yes	6.13	0.08-0.16	-
TER-I 54-IR	getter	Yes	4.11	0.10-0.17	-
TER-V 48-NI	γ-MnO <sub>2</sub>	No	6.92	-	17.1 +/- 0.6
TER-V 48-NI	getter	No	5.99	-	-
TER-V 48-IR	γ-MnO <sub>2</sub>	Yes	3.84	0.08-0.18	-
TER-V 48-IR	getter	Yes	4.21	0.07-0.15	-
QUAT-V 48-NI	γ-MnO <sub>2</sub>	No	5.48	-	16.3 +/- 0.6
QUAT-V 48-NI	getter	No	5.38	-	-
QUAT-V 48-IR	γ-MnO <sub>2</sub>	Yes	4.11	0.06-0.13	-
QUAT-V 48-IR	getter	Yes	3.47	0.29-0.56	-

3  
4  
5  
6  
7  
8  
9

Table 6: Pore structure measurements of BET specific surface areas (by nitrogen sorption-desorption) and porosity (by ethanol saturation) for the reference cement paste from [Lambertin 2010], and for the formulated mortars with γ-MnO<sub>2</sub> or γ-MnO<sub>2</sub>/Ag<sub>2</sub>O getter. In material labels, NI stands for non irradiated and IR for irradiated; different NI and IR mortar samples are characterized at the same age, after irradiation experiments (see Table 3).

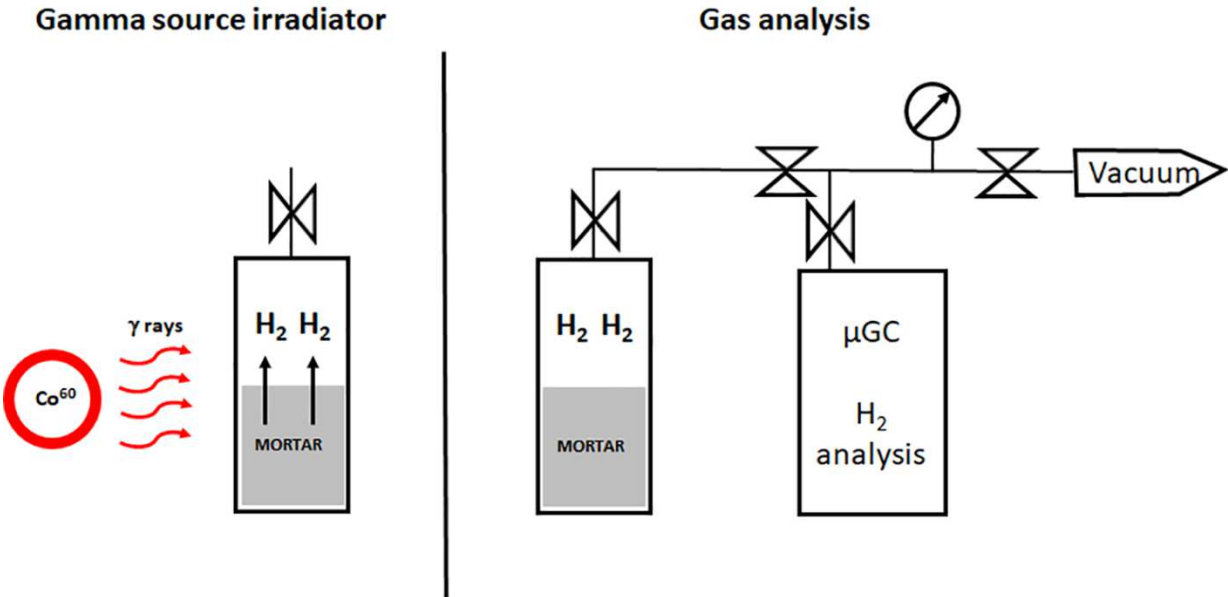
1 **Figures**



2

3 Figure 1: Grain size distributions of  $\gamma$ -MnO<sub>2</sub> (simplified as MnO<sub>2</sub> in the legend),  $\gamma$ -MnO<sub>2</sub>/Ag<sub>2</sub>O  
 4 getter (simplified as MnO<sub>2</sub> + Ag<sub>2</sub>O (getter) in the legend) and of both Type I (CEMI) and Type  
 5 V (CEMV) cements.

6



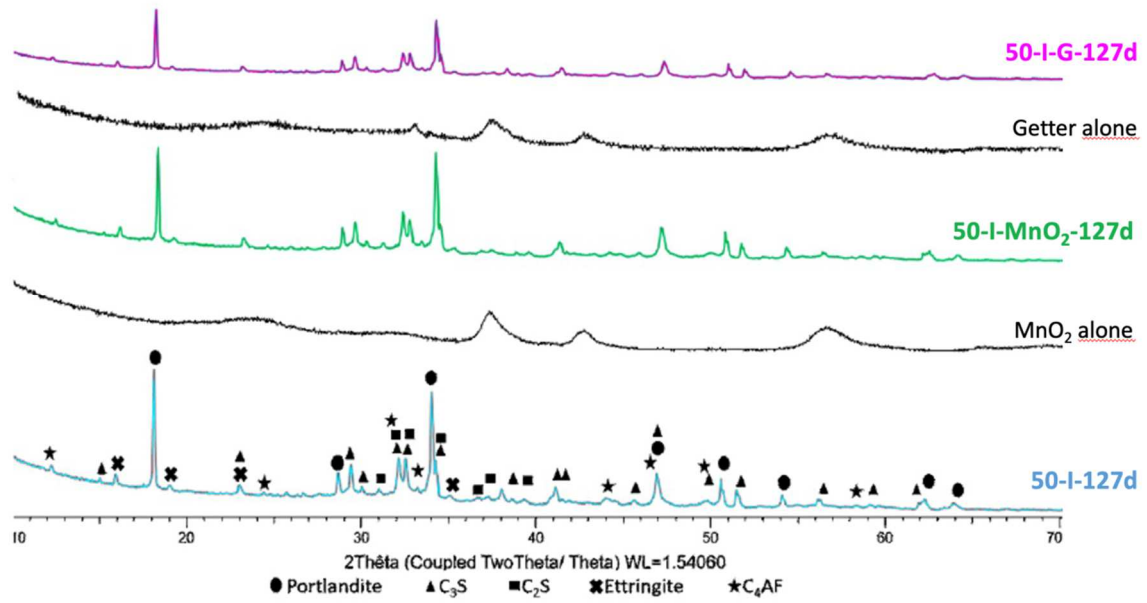
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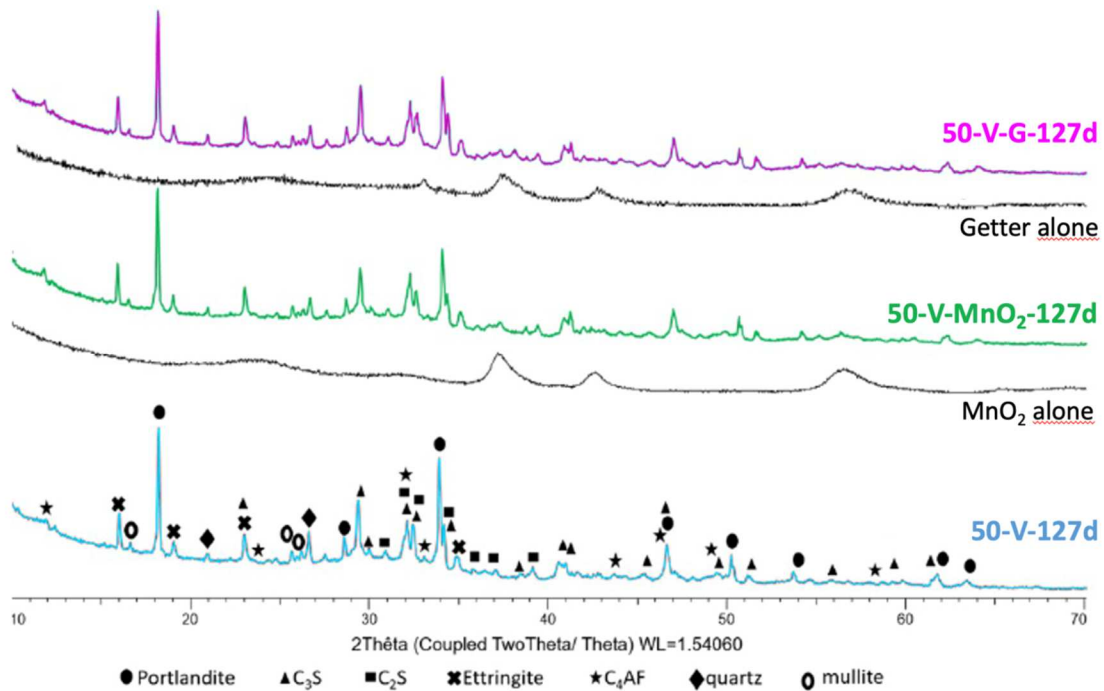
Figure 2: Principle of the gamma irradiation experiment using a <sup>60</sup>Co source. Hydrogen gas is quantified by micro-Gas Chromatography (µGC).

3

4

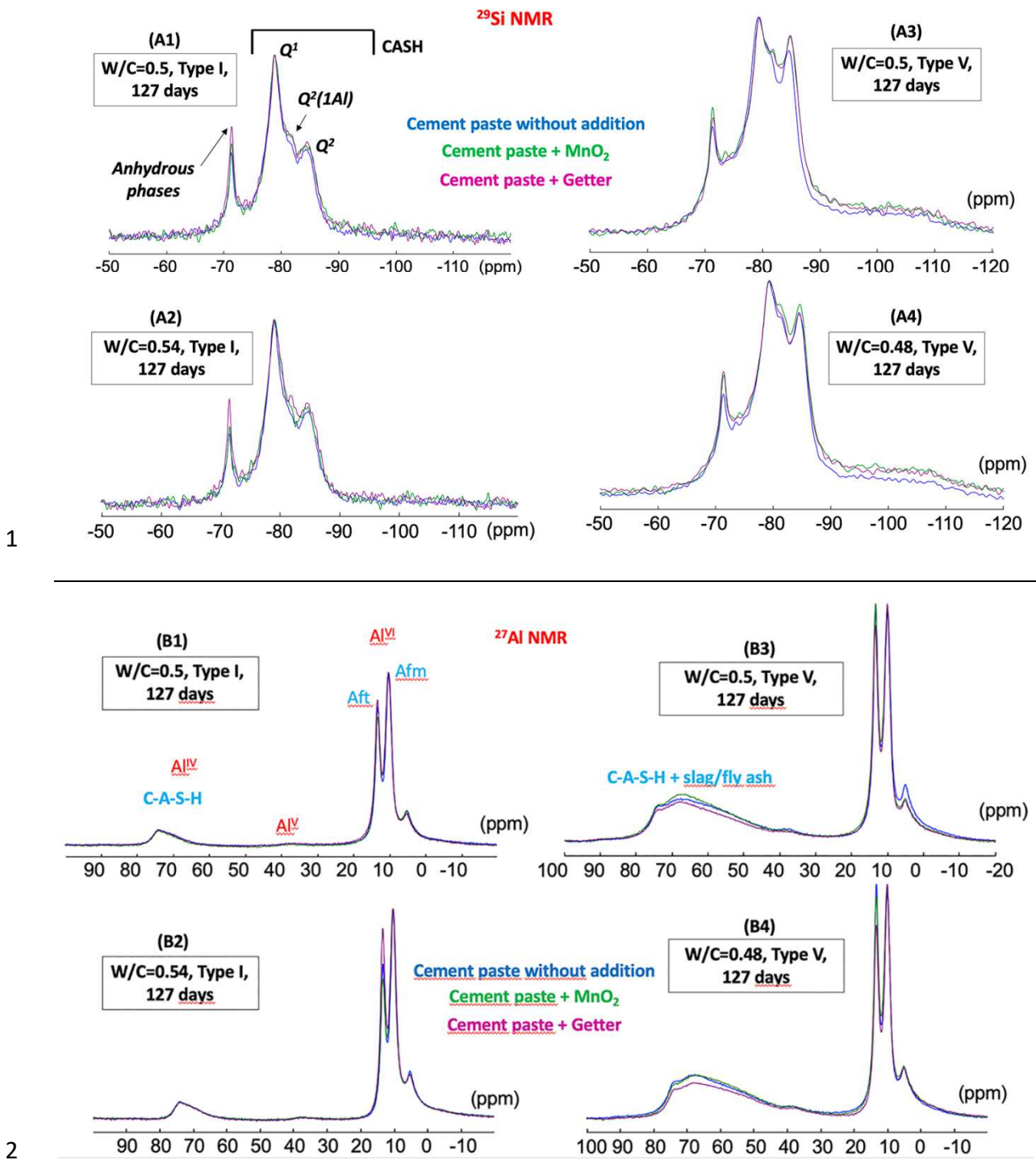


1 (a):



2 (b):

3 Figure 3: XRD results for (a): Type I and (b): Type V cement pastes at W/C=0.5, after 127 days  
 4 endogenous curing at 21°C +/-1 and isopropanol drying, for samples made without or with  $\gamma$ -  
 5 MnO<sub>2</sub> or getter. Phase identification provides portlandite CH (black ellipsoid marks), C<sub>3</sub>S  
 6 (black triangle marks), C<sub>2</sub>S (black square marks), ettringite (black cross marks), C<sub>4</sub>AF (black  
 7 star marks), quartz (black diamond marks) and mullite (hollow ellipsoid marks).



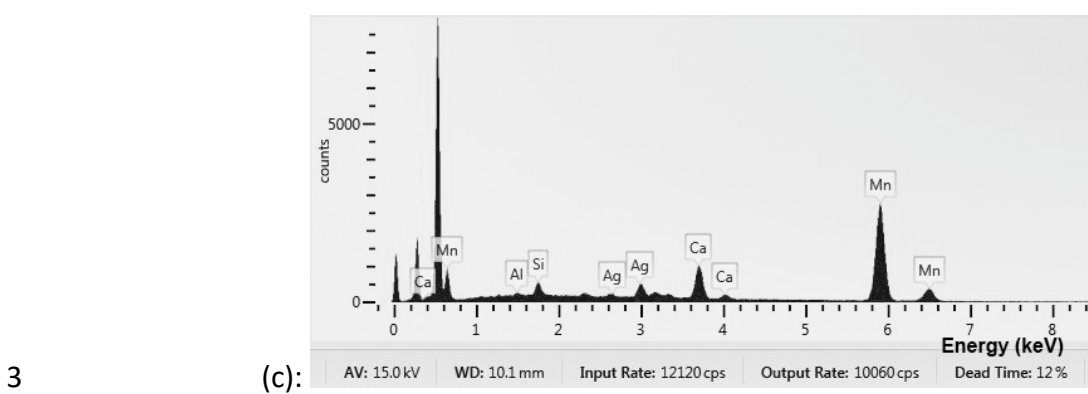
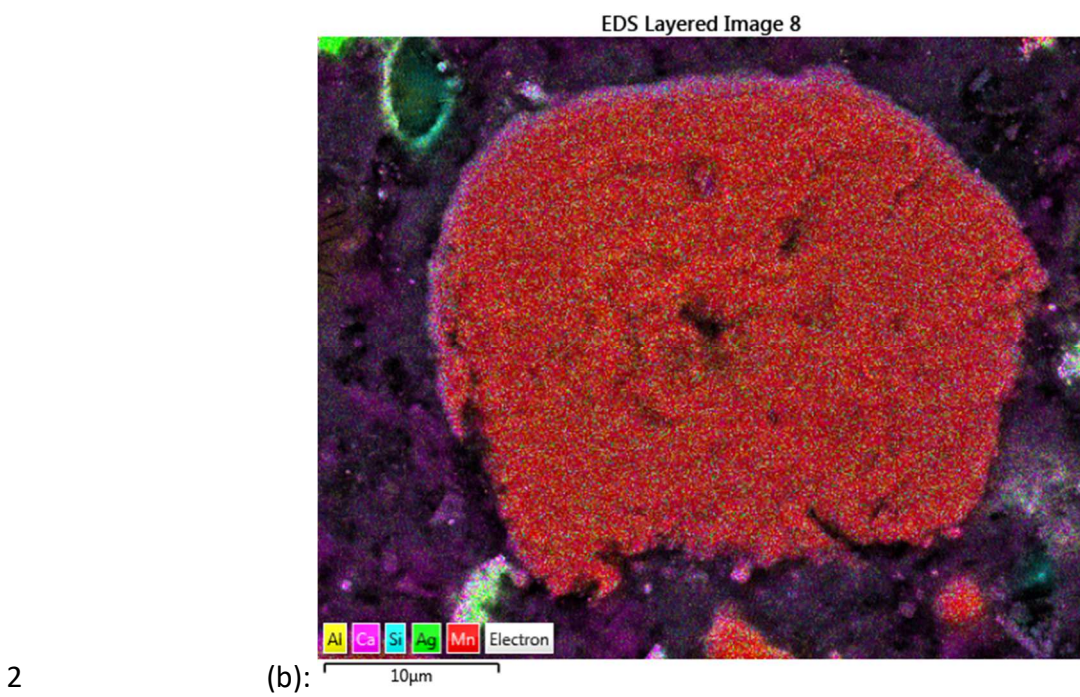
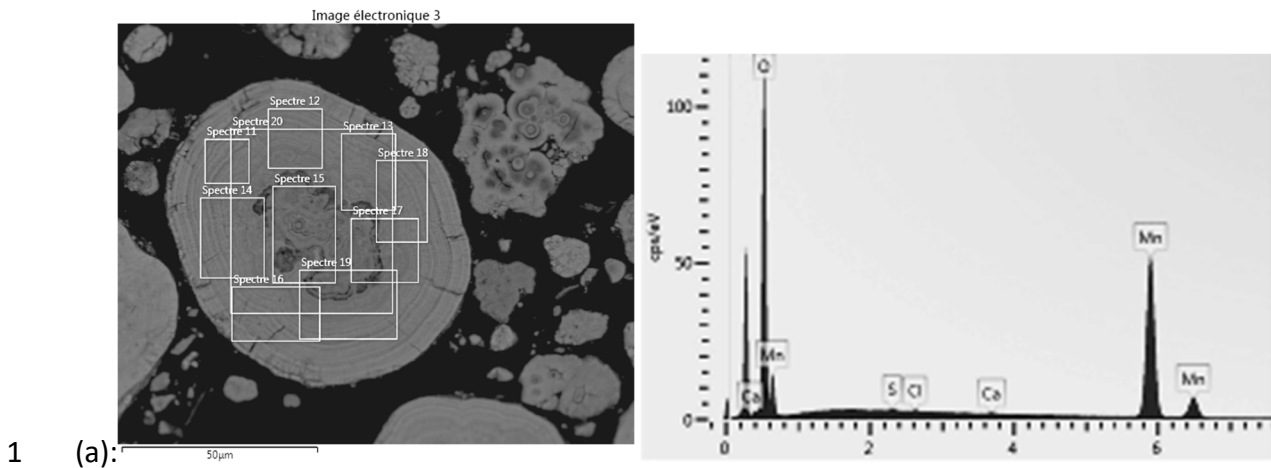
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2

3 Figure 4: MAS NMR results for <sup>29</sup>Si (top graphs, labels A1 to A4) and <sup>27</sup>Al (bottom graphs,  
 4 labels B1 to B4) for CEM I pastes at W/C=0.5 or 0.54 (A1, A2, B1 and B2) and CEM V pastes at  
 5 W/C=0.5 or 0.48 (A3, A4, B3 and B4). Pastes are added with getter (in pink), or  $\gamma$ -MnO<sub>2</sub> (in  
 6 green), or without addition (in blue).

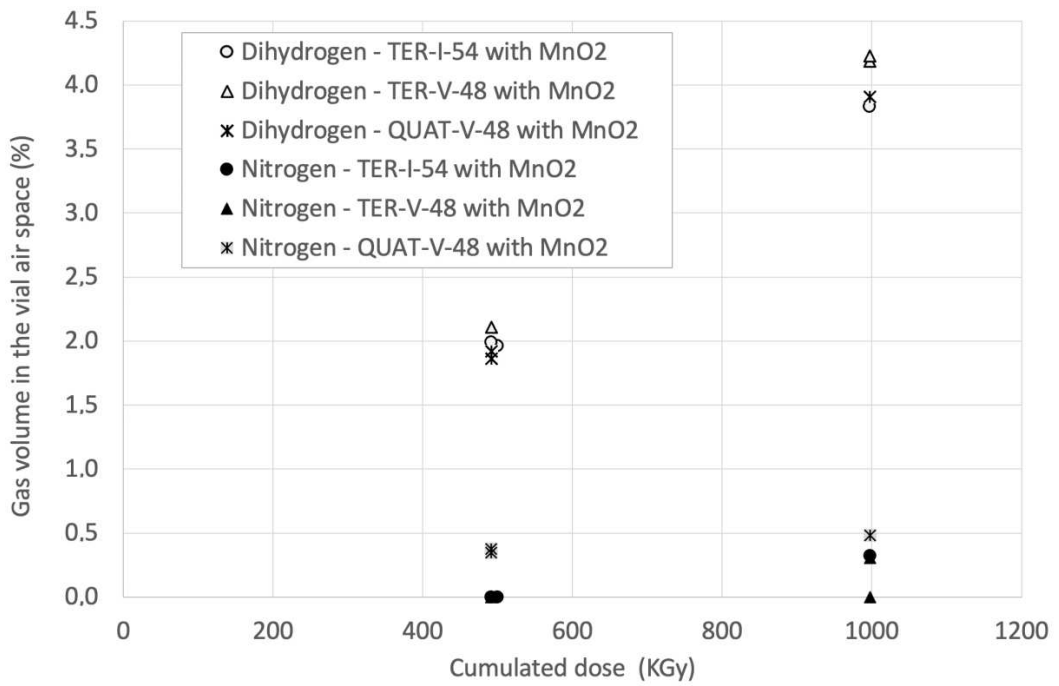
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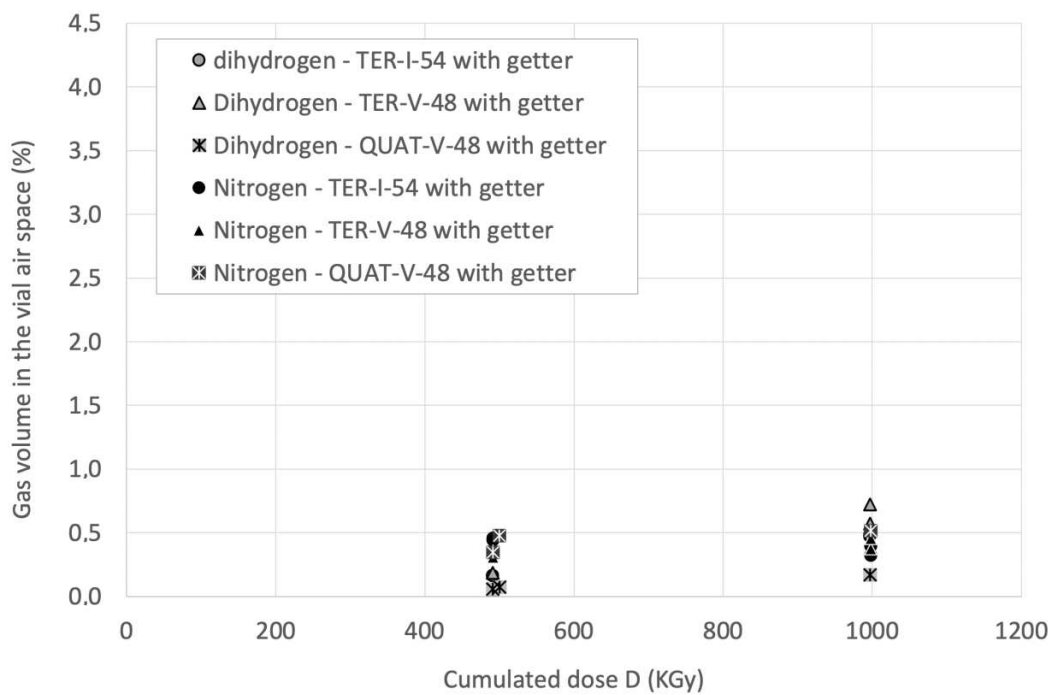


4 Figure 5: (a): SEM observation of a polished getter grain embedded in epoxy resin (left) and  
 5 a typical EDS spectrum corresponding to the rectangular areas visible on the left; (b): SEM  
 6 observation of TER-I-54 mortar (magnification x2700) and (c): Energy Dispersive  
 7 Spectroscopy (EDS) cartography for Al, Ca, Si, Ag and Mn atoms performed over the whole  
 8 grain area.



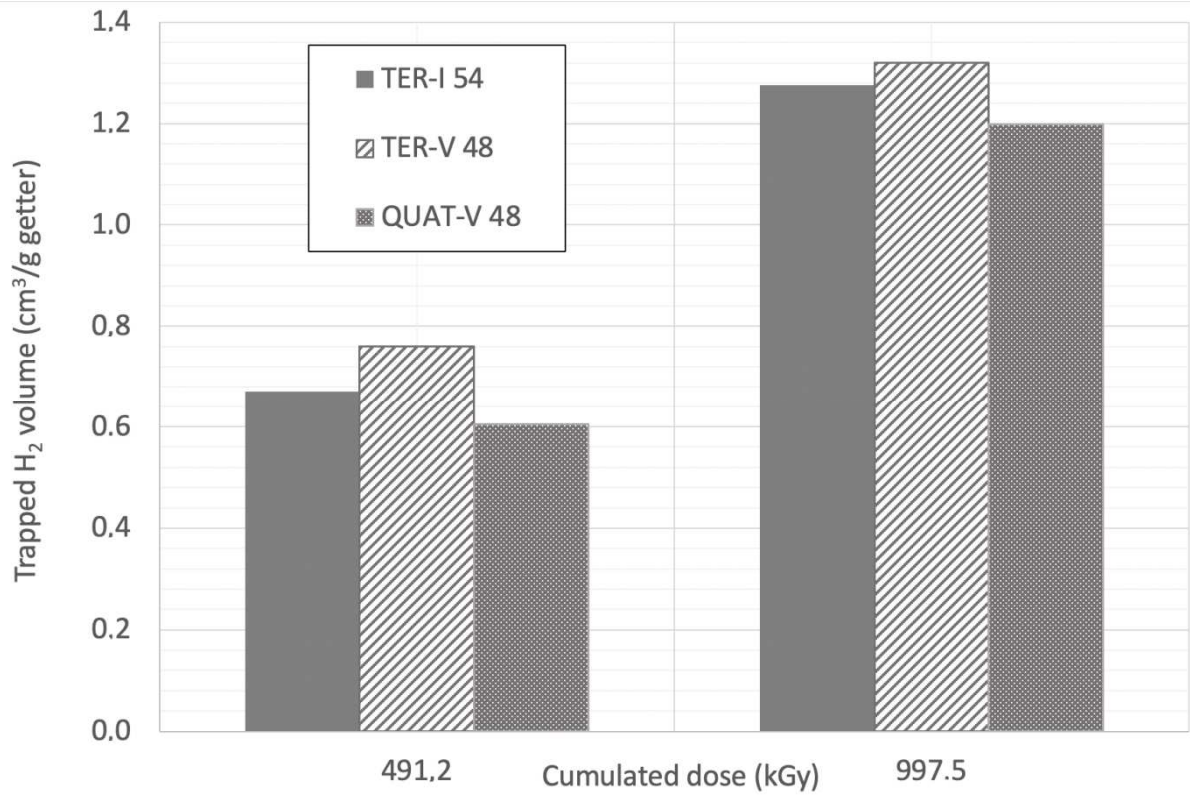


1 (a):



2 (b):

3 Figure 6: Dihydrogen and nitrogen gas volumes produced in the sample vial air space (in  
 4 %vol) for each mortar sample made with (a)  $\gamma$ -MnO<sub>2</sub> or (b) getter, as a function of  
 5 cumulated gamma Ray dose. Dihydrogen data points are labelled with empty circles, and  
 6 nitrogen with black triangles.  
 7



1

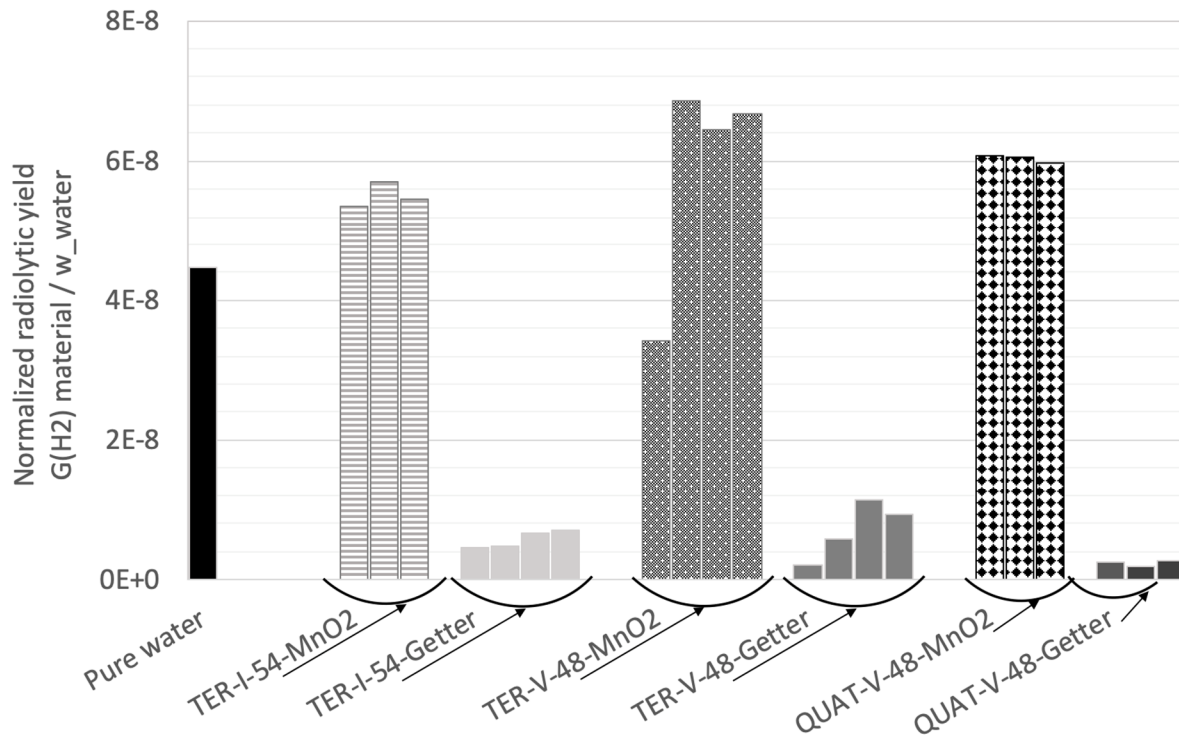
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Figure 7: Trapped H<sub>2</sub> volume expressed in cm<sup>3</sup>/g getter for the three mortar formulations

3

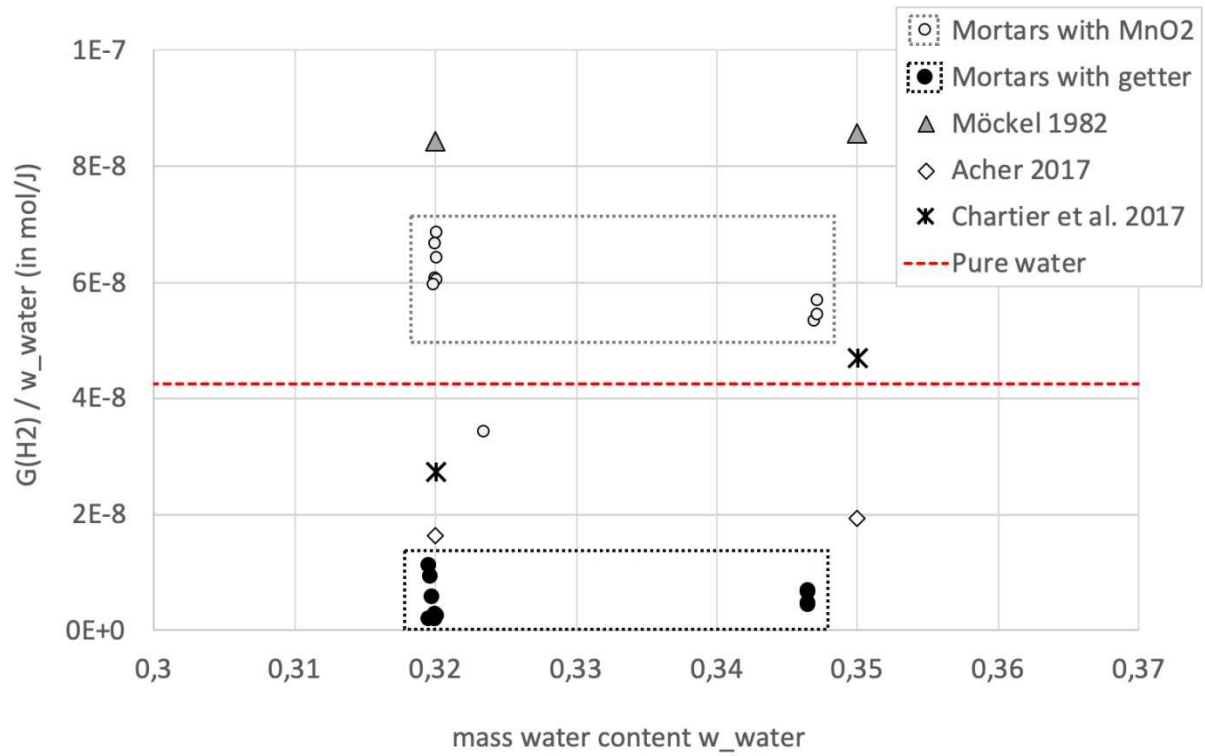
depending on the applied cumulated dose

1



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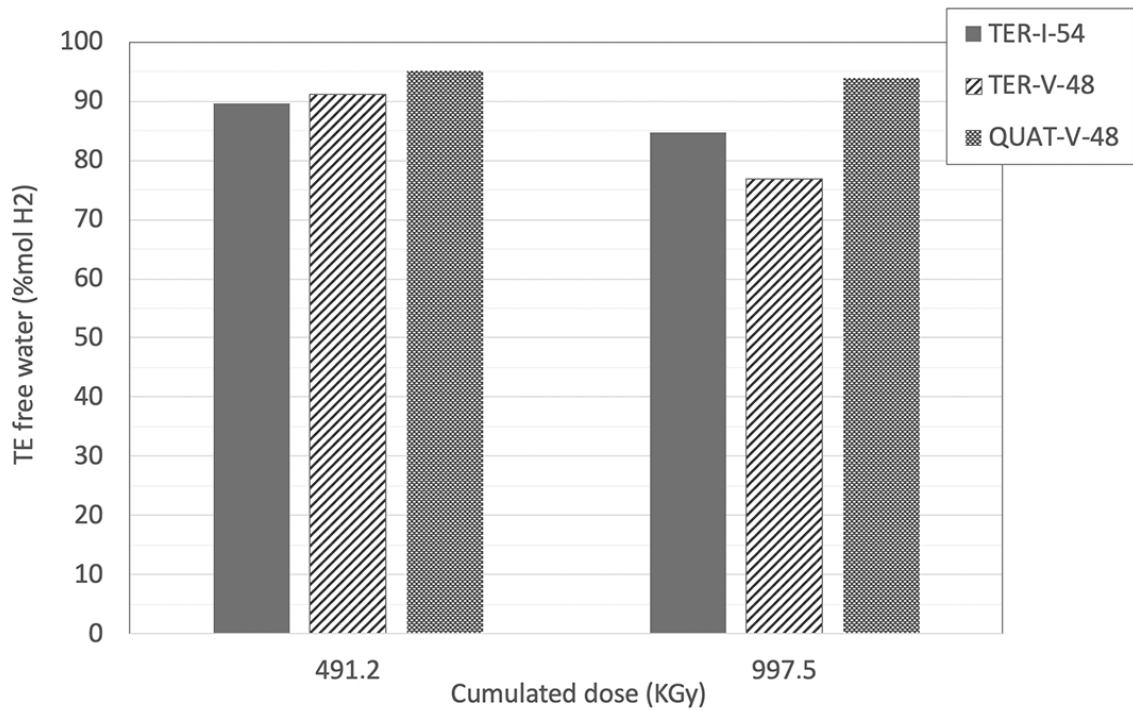
3 Figure 8: Normalized radiolytic yield  $\frac{G(H_2)_{material}}{w_{water}}$  (in mol/J) for mortars made with  $\gamma$ -MnO<sub>2</sub>  
 4 (patterned columns) or getter (uniform columns), compared to the dihydrogen release of  
 5 pure water (black column on the far left), depending on mortar formulation (TER-I-54, TER-  
 6 V-48, or QUAT-V-48) and cumulated dose (per material, first two columns at 491.2 kGy, third  
 7 and whenever possible fourth columns at 997.5 kGy).



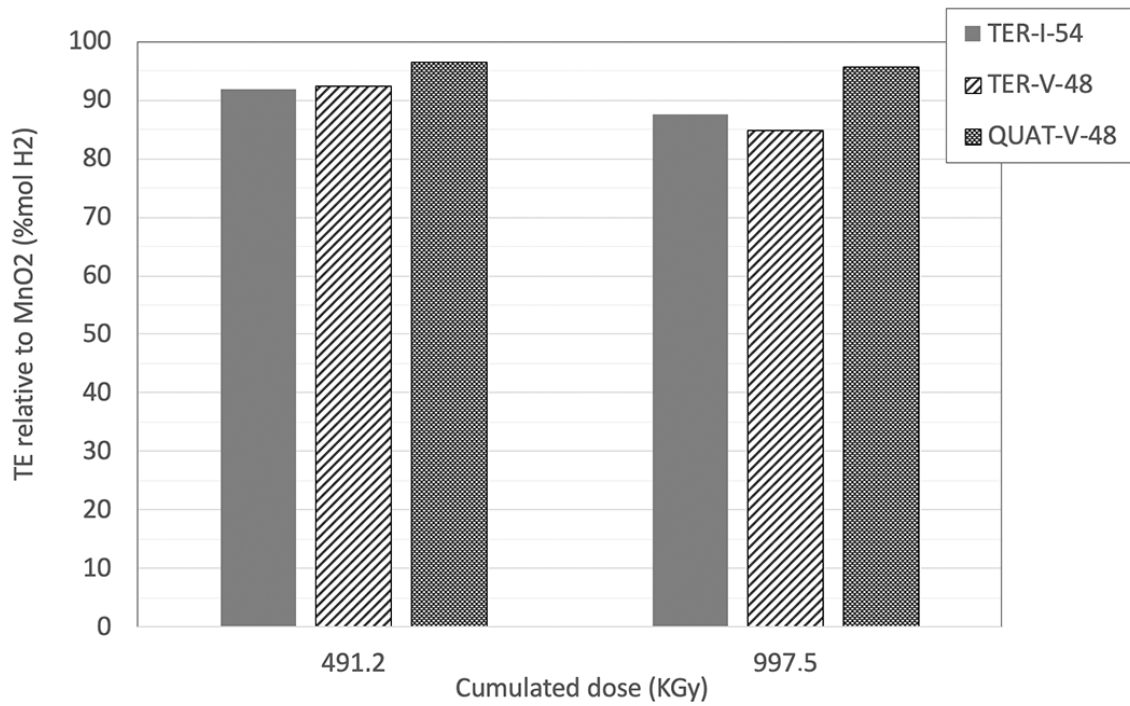
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2 Figure 9: Normalized radiolytic yield  $\frac{G(H_2)_{material}}{w_{water}}$  (in mol/J), for mortars added with  $\gamma$ -MnO<sub>2</sub>  
 3 or getter, compared to values in the literature for Portland cements pastes [Möckel 1982 ;  
 4 Chartier 2017 ; Acher 2018] and for pure water [LaVerne 2009].

5



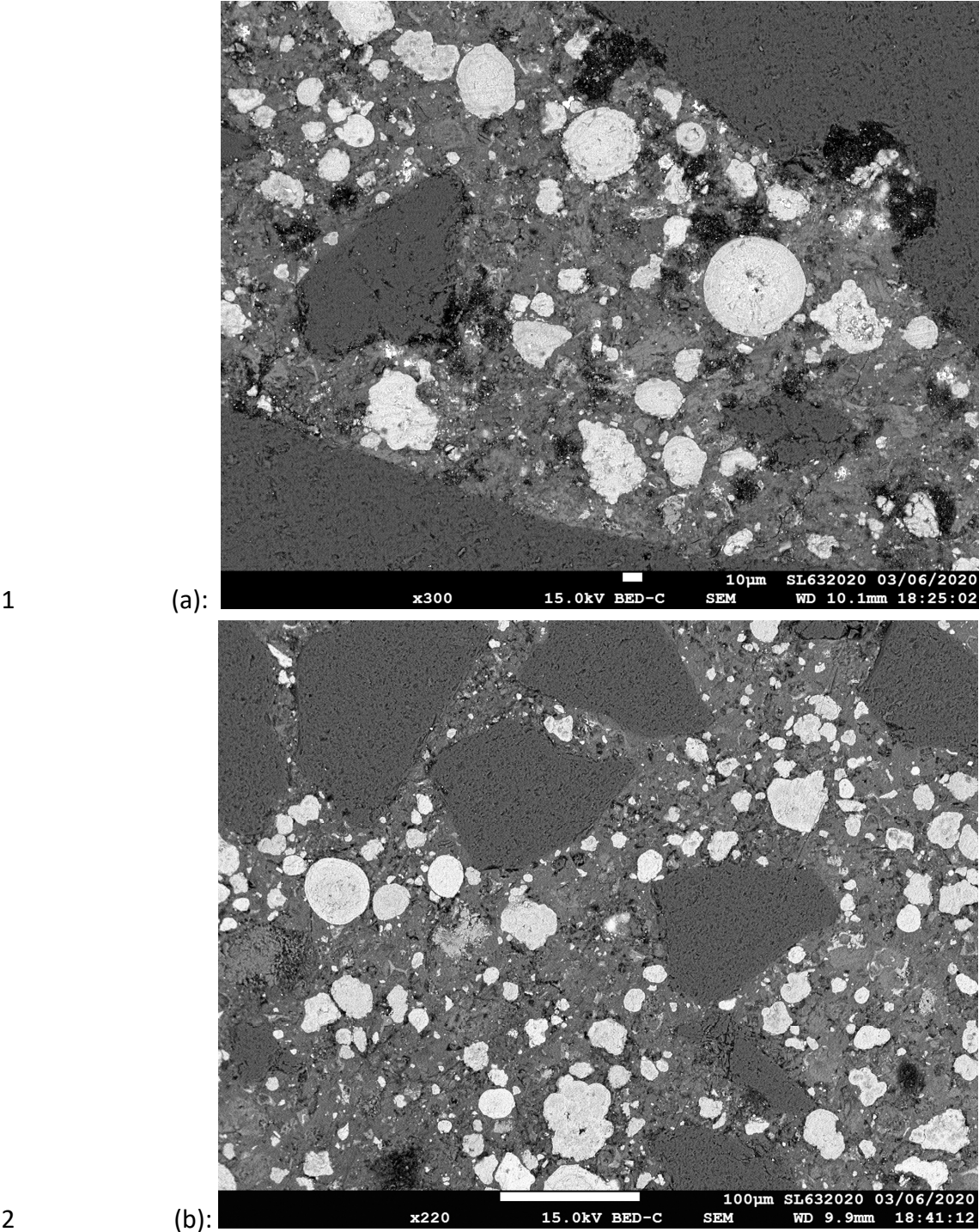
1 (a):



2 (b):

3 Figure 10: Dihydrogen trapping efficiency (a):  $TE_{free\ water}$  (% mol H<sub>2</sub>) and (b):  
 4  $TE_{relative\ to\ MnO_2}$  for the three mortar formulations made with getter ( $\gamma$ -MnO<sub>2</sub>/Ag<sub>2</sub>O) after  
 5 gamma irradiation (in kGy).

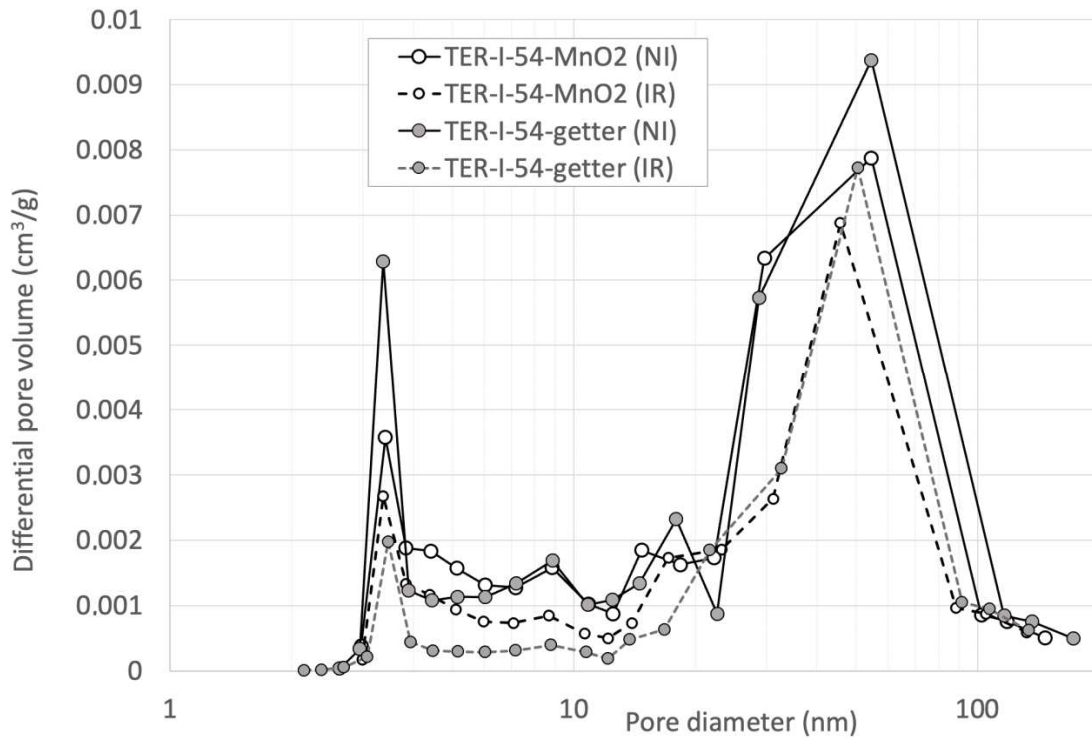




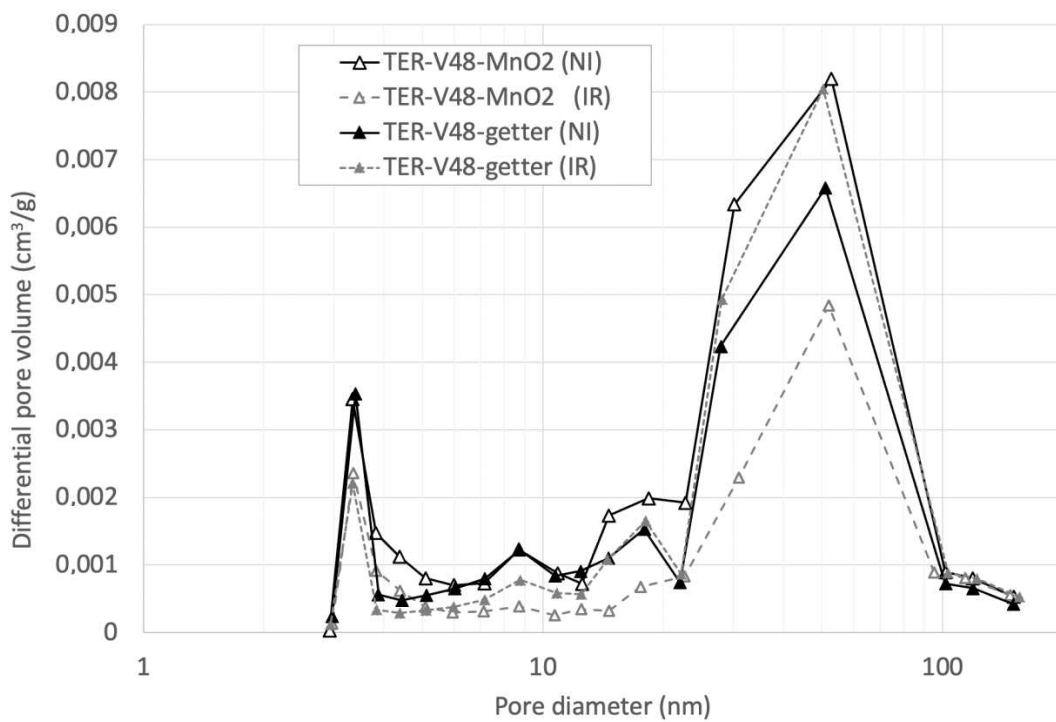
3 Figure 11: SEM observations in BSE mode of (a): TER-I-54 mortar made with  $\gamma$ -MnO<sub>2</sub>/Ag<sub>2</sub>O  
4 getter before gamma irradiation (x300); (b): TER-I-54 mortar made with  $\gamma$ -MnO<sub>2</sub>/Ag<sub>2</sub>O getter  
5 after gamma irradiation (x220).



1



2 (a):



3 (b):

4

5 Figure 12: Pore size distributions of trapping mortars before (NI) and after (IR) 1MGy gamma

6 irradiation, as given by nitrogen desorption for (a) TER-I-54 mortars made with  $\gamma$ -MnO<sub>2</sub> or

7 getter and (b): TER-V-48 mortars. Similar values are obtained for and QUAT-V-48 mortar.