

DEVELOPMENT OF CEMENTITIOUS MATERIALS FOR SUCCESSFUL RADON IMMOBILISATION

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Introduction

The focus of this investigation is on the immobilisation of phosphogypsum (PG) into various cementitious materials. Secondary pollution by the presence of naturally occurring radionuclides (NOR) in PG must be avoided.¹ Therefore, in addition to gamma radiation (regulated for building materials by the European Basic Safety Standards (EU-BSS)²), the presence of radium (further on referring to ²²⁶Ra) as main radionuclide in PG requires particular evaluation of radon exhalation (further on referring to ²²²Rn).³ The radon immobilisation potential of five cementitious materials was assessed, *i.e.* alkali-activated binders, cement and hybrid cement. Alkali-activated binders were composed of ground granulated blast furnace slag (GGBFS) and PG, cement samples were a combination of Ordinary Portland Cement (OPC) and PG, while hybrid cement samples consisted of GGBFS, OPC and PG.

Experimental

GGBFS was derived from a Belgian steel company. CEM I (42.5 N) constituted a commercial cement complying with EN 197-1⁴. PG was an International Atomic Energy Agency (IAEA) reference material (IAEA 434). Prior to sample synthesis, GGBFS was dried in a laboratory oven at 110°C and subsequently milled to a Blaine fineness of $4050 \pm 200 \text{ cm}^2/\text{g}$, determined according to EN 196-6⁵. The density of GGBFS was found 2900 kg/m^3 (Quantachrome Multipycnometer MVP-6DC), determined according to ASTM C204⁶. Both CEM I and PG were used as received. The chemical composition of GGBFS and CEM I was determined by X-ray fluorescence analysis (Philips, PW 1830). The composition of GGBFS was (in wt%): $44.1 \pm 0.2 \text{ CaO}$, $32.5 \pm 0.4 \text{ SiO}_2$, $10.5 \pm 0.7 \text{ Al}_2\text{O}_3$, $8.6 \pm 0.8 \text{ MgO}$ and $1.8 \pm 1.0 \text{ SO}_3$. CEM I constituted of (in wt%): $65.2 \pm 0.1 \text{ CaO}$, $18.3 \pm 0.4 \text{ SiO}_2$, $4.4 \pm 1.1 \text{ Al}_2\text{O}_3$, $1.9 \pm 1.8 \text{ MgO}$, $4.5 \pm 0.6 \text{ SO}_3$ and $3.4 \pm 0.4 \text{ Fe}_2\text{O}_3$. The chemical composition of PG, provided by the IAEA, is (in wt%): $96.0 \text{ CaSO}_4 \cdot 2\text{H}_2\text{O}$, $1.5 \text{ P}_2\text{O}_5$, 1.2 F , 1.0 SiO_2 and $0.2 \text{ Al}_2\text{O}_3$. The activity concentration of ²²⁶Ra in GGBFS, CEM I and PG was determined by gamma spectroscopy with the same procedure as described previously⁷. The solutions were a combination of sodium

hydroxide pellets (grade 99%, supplied by Chem-Lab), sodium silicate (molar ratio $\text{SiO}_2/\text{Na}_2\text{O} = 3.3$ and 65% water, supplied by ABCR GmbH) and distilled water (ASTM type II). Preparation of the solutions was done one day prior to sample synthesis. Five different paste samples were synthesised, Table 1 gives an overview of the sample's composition. The pastes were mixed for 3 min after which they were cast in a silicon mould with dimensions 8.0 cm x 5.5 cm x 2.2 cm. After casting, the mould was wrapped with plastic foil to prevent water evaporation. After 24 h of hardening, samples were demoulded and wrapped with plastic foil, after which they were cured at room temperature and relative humidity 50%. A first series of samples A, B, C, D and E were cured for 4 weeks. A second series of samples A and B were cured for 1, 2, 3, 4 and 12 weeks. After their curing period, samples were dried at 40°C in a laboratory oven till constant weight, after which they were cooled down in a desiccator.

Table 1: Samples' composition

Sample	GGBFS	CEM I	PG	Solution	L/S
A	80	10	10	1 M NaOH	0.5
B	0	90	10	Distilled water	0.5
C	90	0	10	$\text{SiO}_2/\text{Na}_2\text{O} 0.75$; $\text{H}_2\text{O}/\text{Na}_2\text{O} 20$	0.6
D	90	0	10	4 M NaOH	0.6
E	90	0	10	6 M NaOH	0.6

The radon exhalation was determined with a RadonScout PMT radon monitor of SARAD as described previously⁷. The total open porosity (ϕ) (in %) was measured after a curing period of 4 weeks by the difference in mass (in kg) between water-saturated samples (m_s) and samples dried at 40°C in laboratory oven till constant weight (m_d), with:

$$\phi = \frac{m_s - m_d}{v \rho} 100 \quad (1)$$

where v is the sample volume (m^3) and ρ is the water density at 20°C (kg/m^3). Samples were immersed in water at 20°C for no longer than 48 h and until two successive values of mass of the surface-dry sample at intervals of 24 h show an increase in mass of less than 0.5% of the larger value. The samples were made surface-dry by removing surface moisture with a towel.

Results and discussion

The radium activity concentration of GGBFS, CEM I and PG, are 125 ± 11 Bq/kg, 47 ± 2 Bq/kg and 780 ± 62 Bq/kg, respectively. The radium activity concentration is enhanced for PG as a consequence of the chemical similarity between calcium and

radium. The radium activity concentration of the produced samples was calculated based on the ratio's presented in Table 1, and is shown in Table 2.

Table 2: Calculated ^{226}Ra activity concentration of the samples

Sample	A	B	C	D	E
^{226}Ra (in Bq/kg)	183 ± 15	120 ± 8	190 ± 16	190 ± 16	190 ± 16

The radon exhalation of the samples after 4 weeks of curing is shown in Figure 1a. Large differences are observed, although their radium activity concentration was in the same order of magnitude. The radon exhalation of hybrid cement samples was 4 times higher than for cement samples or sodium hydroxide activated binders and even 22 times higher than for sodium silicate activated binders. Sodium silicate activated binders are clearly the best performing immobilisation matrix for radon. The radon exhalation after 1, 2, 3, 4, and 12 weeks of curing for samples A and B is presented in Figure 1b. For hybrid cement samples, the radon exhalation does not vary over time, while the exhalation shows an increase over time for cement samples as a consequence of their continuous microstructural development. The discrepancy between cement and hybrid cement samples is most likely caused by the occurrence of different hydration products and should be elucidated further. The radon exhalation over time of alkali-activated binders should also be investigated, since the hydration of unreacted GGBFS particles is an ongoing process as well.⁸

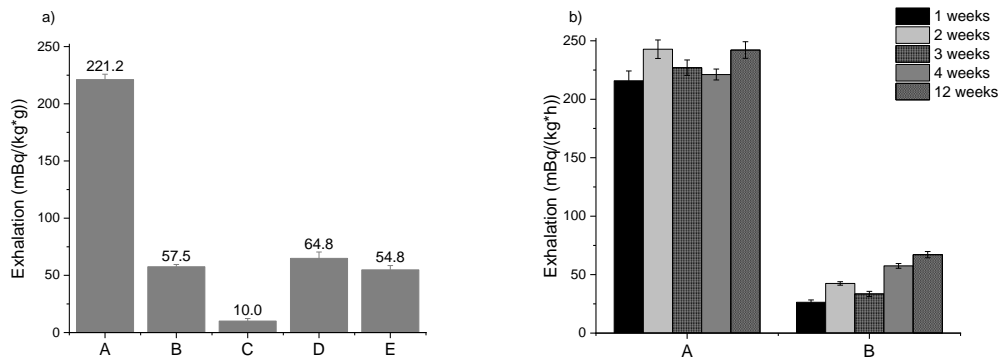


Figure 1: Radon exhalation a) after 4 weeks of curing and b) after 1, 2, 3, 4 and 12 weeks of curing for samples A and B

The results of the water absorption test (in %) after 4 weeks of curing, calculated with Equation 1, are presented in Figure 2. Largest ϕ was found for hybrid cement and cement samples, while alkali-activated binders showed generally lower values. The lowest ϕ was found for sodium silicate activated binders. Radon exhalation vs. ϕ after 4 weeks of curing displays low correlation ($R^2 = 0.7$). The water absorption test cannot discriminate between different pore sizes or shapes, therefore these results should be elucidated further by *e.g.* gas adsorption porosimetry.

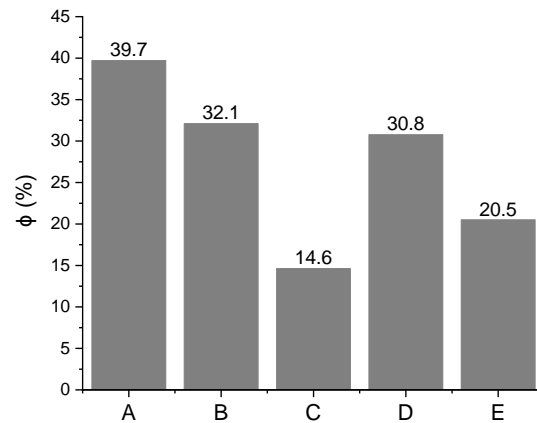


Figure 2: Total open porosity (ϕ) after 4 weeks of curing

Conclusions

In this investigation radon exhalation shows low correlation with the total open porosity, with lowest exhalation and porosity achieved for sodium silicate activated binders. Radon immobilisation was the least successful for hybrid cement samples. For cement samples, the radon exhalation was increasing over time. Further study should focus more in depth on the pore structure and specific surface area evolution and their influence on radon release, in parallel with other effects such as freeze-thaw or carbonation. Additionally, the radon exhalation over time of alkali-activated binders forms a subject of future research as well.

References

1. C.R. Cánovas, F. Macías, R. Pérez-López, M.D. Basallote, R. Millán-Becerro, "Valorization of wastes from the fertilizer industry: Current status and future trends", *J Clean Prod*, **174** 678-690 (2018).
2. Council of the European Union, "Council directive 2013/59/EURATOM: European Basic Safety Standards (BSS) for Protection against Ionising Radiation", *Off J Eur Union*, **L 13/1** (2014).
3. M.P. Campos, L.J.P. Costa, M.B. Nisti, B.P. Mazzilli, "Phosphogypsum recycling in the building materials industry: Assessment of the radon exhalation rate", *J Environ Radioact*, **172** 232-236 (2017).
4. Bureau voor Normalisatie (NBN), EN 197-1: Composition, specifications and conformity criteria for common cements, 2011.
5. Bureau voor Normalisatie (NBN), EN 196-6: Methods of testing cement - Part 6: Determination of fineness, 2010.
6. ASTM International, ASTM C204-17: Standard test methods for fineness of hydraulic cement by air-permeability apparatus, 2017.
7. K. Gijbels, R. Ion Iacobescu, Y. Pontikes, N. Vandevenne, S. Schreurs, W. Schroeyers, "Radon immobilization potential of alkali-activated materials containing ground granulated blast furnace slag and phosphogypsum", *Constr Build Mater*, **184** 68-75 (2018).
8. M. Ben Haha, G. Le Saout, F. Winnefeld, B. Lothenbach, "Influence of activator type on hydration kinetics, hydrate assemblage and microstructural development of alkali activated blast-furnace slags", *Cem Concr Res*, **41** 301-310 (2011).