



# Comparing the short-term leaching behaviour of cements containing supplementary cementitious materials in different leachants for low-level waste encapsulation

A. Kozłowski<sup>1\*</sup>, T. Peshkur<sup>1</sup>, J. C. Renshaw<sup>1</sup>, K. J. Dobson<sup>1,2</sup> and F. Taylor<sup>3</sup>

<sup>1</sup> Department of Civil and Environmental Engineering, University of Strathclyde, 75 Montrose Street, Glasgow G1 1XJ, UK

<sup>2</sup> Department of Chemical and Process Engineering Engineering, University of Strathclyde, 75 Montrose Street, Glasgow G1 1XJ, UK

<sup>3</sup> Nuclear Waste Services, Pelham House, Pelham Drive, Calderbridge, Seascale, Cumbria CA20 1DB, UK

ORCID iD: AK, 0000-0001-7832-4839; JCR, 0000-0003-2073-3239; KJD, 0000-0003-2272-626X

\* Correspondence: [andrea.kozlowski@strath.ac.uk](mailto:andrea.kozlowski@strath.ac.uk)

**Abstract:** Pulverized fly ash (PFA) is commonly used as a supplementary cementitious material (SCM) in cement and is permitted for use in cements and grouts used for the encapsulation of low-level nuclear waste. However, with a global decrease in availability of PFA predicted in the near future, alternative SCMs are required. In nuclear encapsulation, a key parameter for a new SCM is that it does not change the leaching behaviour of the grout. We present promising initial leaching data from two SCMs: metakaolin and waste paper fly ash. These were tested for 24 h in two leachants, deionized water and an artificial groundwater, tracking the pH and leachability of a range of elements as the samples equilibrated with the leachants. The study suggests that for many elements, both metakaolin and waste paper fly ash show a very similar leaching behaviour to PFA grout formulations despite differences in the pH equilibration. In general, the tests suggest that the composition of the elute is dominated by leaching from the cementitious phases, and not the SCM. This suggests that further longer-term leaching studies are required as part of testing for SCM suitability for nuclear grouts in order to understand the connections between leaching and grout microstructure.

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As of April 2022, approximately 94 vol% of all nuclear waste in the UK is categorized as low-level waste (LLW) or very low-level waste (VLLW) (BEIS and NDA 2022). This type of waste is immobilized by the Nuclear Waste Services in the UK in grout that comprises a 3 : 1 mix of pulverized fly ash (PFA) and ordinary Portland cement (OPC). PFA is been used historically for the encapsulation of LLW (Atkins and Glasser 1992; Glasser 1992; Wilding 1992; Sear 2001; Sharp *et al.* 2003; National Research Council 2011; Ojovan 2011). PFA is a fine waste produced in coal-fired power stations and is used as a supplementary cementitious material (SCM) (Collier and Tearle 2020). As UK Net Zero legislation will see all coal-fired power stations close by 2025 (BEIS 2018; UK Government 2019), an alternative SCM that gives the grout the same (or better) mechanical and chemical properties is required.

Local sources of PFA for radioactive waste conditioning and containment have already been eliminated, and UK radioactive waste management organizations currently procure PFA from overseas. Essential properties of PFA include:

- maintaining a pH of *c.* 11;
- the grout not releasing unacceptable quantities of hazardous substances or non-hazardous pollutants; and
- the grout having consistent and reliable properties (both physical and chemical) (Paulley *et al.* 2020).

As the end of coal-fired power plants is also planned elsewhere (Deutsche Bundesregierung 2020; Huttunen *et al.* 2022; Katinas 2023; UNFCCC 2023), LLW cement formulations must be changed (Zhou *et al.* 2006; Covill *et al.* 2011) or the PFA must be replaced

with other SCMs while maintaining the same overall grout formulation (3 : 1 SCM : OPC). Alternative SCMs need to be available in large volumes and over decades, and ideally have low CO<sub>2</sub> emissions.

In this study we tested biomass fly ash (BMFA), beneficiated pulverized fly ash (BPFA), which is a waste combustion ash that is processed for further use (Cammarota *et al.* 2008), metakaolin (MK), olivine (OL), pozzolanic sand (PS), volcanic ash (VA) and waste paper fly ash (WPFA). In industry, waste paper fly ash is usually abbreviated as PFA; however, in this paper, WPFA is used to distinguish it from pulverized fly ash.

Studies on SCMs have looked at the impact of the percentage of SCM in the grout formulation on the compressive strengths of the grout (Siddique 2012; Contrafatto *et al.* 2020; Meko and Ighalo 2021; Olatoyan *et al.* 2023; Akash Kanna and Parthasarathi 2024), and have showed for BMFA and WPFA that fluctuations in the origin of the fuel and source of the materials can affect its performance (Maschowski *et al.* 2020; Meko and Ighalo 2021; Baloochi *et al.* 2022). Other studies have looked at leaching behaviour and have shown the importance of the leachant, with element release from OPC, PFA, WPFA, BMFA and MK being controlled by fluid composition and acidity (Du *et al.* 2014; Hartwich and Vollpracht 2017). Studies have highlighted the leaching of Ca, as well as Fe, Cu and Mn (Akar *et al.* 2012; Eskander *et al.* 2013; Berra *et al.* 2019; Sun *et al.* 2019; Baloochi *et al.* 2022). By using SCMs in nuclear waste encapsulation, some of the potentially leachable elements may have significant environmental toxicity (e.g. B, Cr, Se and W), while the leaching of other elements (e.g. Al, Fe, Mg and Ti) may cause a deterioration

of the mechanical properties over time (Haga *et al.* 2005; Jebli *et al.* 2018; Tian *et al.* 2018; Jin *et al.* 2022; Ma *et al.* 2022; Yang *et al.* 2023; Zheng *et al.* 2023).

Of interest for this study are the performances of the examined grouts in accordance with maintaining the pH level and the release of elements. In this research programme, we investigated different time spans (ranging from 24 h to 1 year) and present here the results of the 24 h studies. Understanding the release of elements across all timescales is necessary for assessing safety cases (Huntington 2016). This includes the behaviour of an element that comes into direct contact with an eluent.

## Methodology

Because of the importance of leachant acidity on element mobility, this study was focused on element leachability in deionized water (DW) and an artificial groundwater (GW) from two potential SCMs (MK and WPFA), and these were compared to unamended OPC and the industry standard PFA formulation. Our static experiment was adapted from ASTM C1308-21 and ASTM C1220-21 (ASTM 2021a, b) in order to provide information on the leaching behaviour of cements and the mobility of key elements, such as Ca, Na and K, in an SCM–water system. The artificial groundwater used in this study was based on the formulation used in May *et al.* (2012) (see Table A1 in Appendix A), which represents the groundwater found at a UK LLW storage site at Drigg.

The OPC only (Tarmac, UK) formulation comprised 100% OPC, and the PFA (Tarmac, UK), MK (AGS Mineraux, France) and WPFA (Saica, Spain and UK) grout formulations were mixed at a ratio of 3 : 1 (SCM : OPC) following AMST C192/C192-M (ASTM 2020). We used a superplasticizer (Sika ViscoCrete-150 PF: 1.03 kg l<sup>-1</sup>) to water ratio of 2.43% (except for WPFA: 2.13%) and the liquid/solid mass ratios used were: OPC, 0.31; PFA, 0.28; MK, 1.50; and WPFA, 1.27. All samples were left to set for 48 h in silicone moulds at ambient conditions. After demoulding they were rinsed with DW to remove surface bleeding residues, and then wet cured at 20°C, 100% humidity for 21 days using standard procedures. Samples were then left to dry at ambient room conditions and stored under the same conditions until used.

Leaching was performed on three 10 × 10 × 25 mm cuboids cut from each sample, with each aliquot submerged individually in DW at 20°C or in GW at 5°C (all with liquid/solid ratio of 10 in 125 ml LDPE bottles) for 24 h. The pH was measured prior to the addition of the sample, and the pH was then measured automatically (Environmental Express, pH electrode, Refillable, WZ-05992-30) at 5 min intervals for the first hour and then at 15 min intervals for the remaining 23 h.

For elemental analysis, 11 ml of the liquid was extracted after 24 h and filtered with 0.45 µm cellulose acetate filter. Then 10 ml was acidified with 0.05 ml of HNO<sub>3</sub> for inductively coupled plasma optical emission spectroscopy (ICP-OES) (Thermo Scientific iCAP 6000 Series) of all aliquots for each sample, and the mean and standard deviation (1σ) were determined. The aliquots were tested for the elements (including the wavelength): Al (3961 nm), Ca (3179 nm), Fe (2382 nm), K (7664 nm), Mg (2593 nm), Na (5895 nm), S (1820 nm), Si (2124 nm) and Ti (3234 nm). The appropriate DW and GW specific background (BG) corrections were applied (see Table A3 in Appendix A). The final 1 ml of the extracted liquid was replenished with nano-pure water (18.2 Ω) to a dilution factor of 10 for ion chromatography (or ion-exchange chromatography: IC).

Anion analysis of Br<sup>-</sup>, Cl<sup>-</sup>, F<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>-</sup> and PO<sub>4</sub><sup>-</sup> (using MagIC Net 3.3 software) was performed by IC (Metrohm 850 Professional IC and Metrohm 858 Professional Sample Processor). For the bulk composition of the unleached samples, the grout samples were digested by microwave-assisted extraction (MAE) using a CEM

MARS-6 system prior to analysis by ICP-OES. Unleached samples of each material were crushed (0.1063 g OPC, 0.1060 g PFA, 0.1027 g MK and 0.1078 g WPFA), and then pre-digested with 8 ml of HCl and 2 ml of HNO<sub>3</sub> for 15 min. The samples were then microwaved at 1800 W, 20 min ramp time at 175°C, 25 min hold time at 200°C. After microwaving, the digested samples were diluted to 100 ml with nano-pure water (18.2 Ω) and filtered through a 0.45 µm cellulose acetate filter before compositional analysis. These compositional data were used to define the extracted yields in the leached samples as a percentage (equation 1). The MAE of the crushed samples is used to define the theoretical maximum extraction yield to which the ICP-OES results of the examined examples are related and presented as the total possible percentage (% tot.). The extraction yields were calculated using equation (1):

$$\%_{\text{tot.}} = \frac{C_{\text{EI}} - C_{\text{W}}}{C_{\text{MAE}}} \times 100\% \quad (1)$$

where  $C_{\text{MAE}}$  represents the bulk digestion results,  $C_{\text{EI}}$  represents the leachate ICP-OES results and  $C_{\text{W}}$  represents the ICP-OES results of DW or GW.

## Results

### pH

The DW had an initial pH of 5.86 ± 0.14, while the GW had an initial pH of 8.66 ± 0.63.

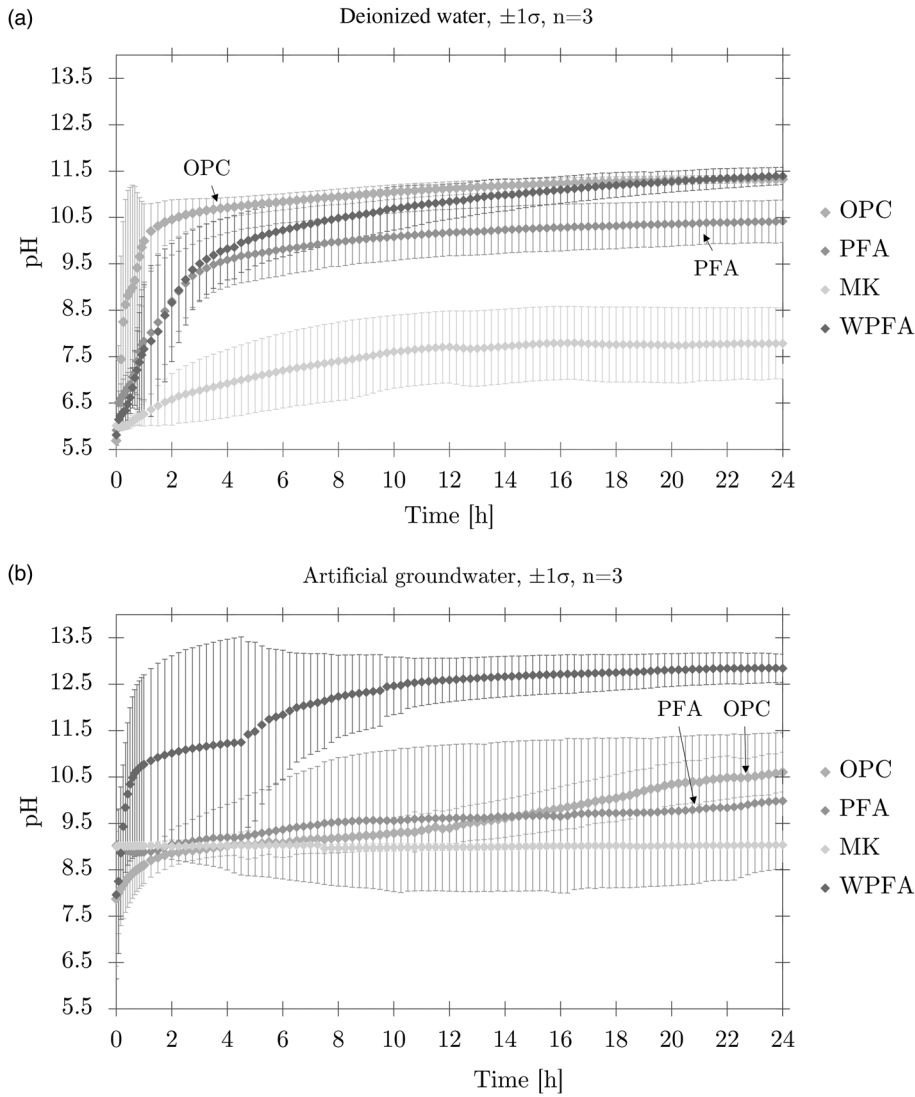
#### Ordinary Portland cement

The 100% OPC sample in DW equilibrated in three main steps (Fig. 1a). In the first 15 min, the pH increased rapidly from 5.69 ± 0.02 at 0 h to 8.25 ± 2.16 at 15 min. The increase in pH then ran fairly linearly for the next 15 min (pH<sub>30 min</sub> = 8.91 ± 2.23), followed by an exponential increase, with the pH reaching 11.33 ± 0.07 at 24 h. The standard deviation (σ) was rather high – between 1.23 and 2.26 – at the beginning (up to 50 min) of the experiment and then decreased exponentially, reaching σ<sub>24 h</sub> = 0.07.

By comparison, the GW system did not show the same initial rapid increase in pH but instead had a slower initial rate and an earlier shift from rapid to slower increase that occurred gradually over a 2 h period, the pH then followed a near linear increase to the final pH of 10.61 ± 0.43 after 24 h, with a slight acceleration in the rate of increase from 12–18 h (Fig. 1b). In the GW the OPC still had to reach equilibrium, although the data from 20 h suggest that it may have been approaching it. The total change in pH for the GW system was only 2.7, compared to 5.64 in DW.

#### Pulverized fly ash

The pH of the PFA sample in DW had the same general form as the OPC sample but increased more slowly over the initial rapid phase and increased steadily in two steps in the first 3.5 h: from pH 5.91 ± 0.03 to pH 7.61 ± 1.01 after 50 min, followed by a slight decrease of steepness to pH 9.49 ± 0.62 (at 3.5 h; Fig. 1a). The pH then only increased slightly, reaching pH 10.42 ± 0.46 after 24 h, which is roughly 1 pH unit less than the OPC. The standard deviation showed some variety within the triplet examined. Whilst σ increased slightly in the first 40 min, it was followed by a rapid increase up to σ = 1.32 (at 1.25 h), which immediately decreased exponentially after this time until settling at around σ = 0.46 (at 24 h). As in DW, the PFA grout showed the same general form as the OPC sample in GW; Figure 1b. Two main differences could be observed. First, the averaged pH decreased slightly in the first hour from 9.02 ± 0.10 to 8.88 ± 0.02. For two samples of the triplet, this behaviour occurred. The other sample increased by 0.2 pH units in 10 min and decreased linearly (0.1 pH unit per 5 min) for 55 min.



**Fig. 1.** pH evolution of grout formulations in (a) deionized water and (b) artificial groundwater. OPC, ordinary Portland cement; PFA, OPC + pulverized fly ash (1 : 3); MK, OPC + metakaolin (1 : 3); WPFA, OPC + waste paper fly ash (1 : 3). Mean and  $1\sigma$  standard deviation ( $n = 3$ ).

The standard deviation was low ( $\sigma < 0.10$ ) at the start but then increased significantly within the first 2 h and remained constant over the linear portion of the curve. This is due to sample 1 of the triplet, which showed a decreasing behaviour for 1 h before the same pH behaviour occurred compared to the other two samples, thus affecting  $\sigma$ . Second, the increase in the rate of the PFA is lower than that of the OPC, resulting in a lower pH compared to the OPC by  $\Delta = 0.6$  pH units.

#### Metakaolin

MK behaved differently to all of the other examined samples. Its pH after 24 h in DW was much lower than all other observed grouts ( $\text{pH}_{\text{MK}} = 7.79 \pm 0.76$ ,  $\text{pH}_{\text{PFA}} = 10.42 \pm 0.46$ ,  $\text{pH}_{\text{OPC}} = 11.33 \pm 0.07$ ,  $\text{pH}_{\text{WPFA}} = 11.40 \pm 0.18$ , all at  $t = 24$  h; Fig. 1a). Further, whilst all of the other three observed grouts had a rapid increase within the first 4 h, the pH of the MK increased slowly for 12 h ( $\text{pH} 7.71 \pm 0.78$ ) and then the pH marginally fluctuated at around pH 7.79 until the end of the experiment. The standard deviation increased gradually from  $\sigma_{0\text{h}} = 0.14$  to  $\sigma_{8.25\text{h}} = 0.85$ , after which  $\sigma$  remained fairly constant at around  $\sigma_{8.5-24\text{h}} = 0.8$ .

For MK in GW, small fluctuations of the pH were visible – staying constant throughout the observed time period at around pH 9 (Fig. 1b). The maximum standard deviation for the all measurements was  $\sigma_{\text{max}} = 0.09$ . Compared to the OPC, a similarity could be observed: between 2 and 7 h, the pH of the OPC and the MK were nearly the same. The main difference was that although the pH of

the MK remained almost stable throughout the whole 24 h, the pH of the OPC increased until  $t = 2$  h and then continued to increase throughout the time, leading to a difference in pH between the MK and the OPC of  $\Delta = 1.6$  pH units.

#### Waste paper fly ash

The WPFA in DW showed similar equilibration behaviour to the PFA (Fig. 1a). In the first hour, the pH of the WPFA was slightly lower than that of the PFA. Between 1 and 2.25 h the increase in the pH of the WPFA was very similar to that of the PFA. Differences appeared from  $t = 2.25$  h onwards, when the WPFA had a constantly higher pH than the PFA and was approaching the pH behaviour of the OPC. The WPFA pH overlapped with the OPC pH after 21 h but continued to increase, reaching a pH of  $11.40 \pm 0.18$  after 24 h. The standard deviation was  $\sigma < 0.5$  for the first 40 min and then increased steeply to  $\sigma_{1.5\text{h}} = 1.64$ , followed by a significant decrease over the remaining 24 h ( $\sigma_{24\text{h}} = 0.18$ ).

Contrary to the similarity between the WPFA and the PFA/OPC in DW, the WPFA behaved differently in GW, specifically in the first 12 h (Fig. 1b). After 15 min, the pH of the WPFA was higher than for all of the other observed grouts and continued to be so until the end of the experiment. After 12 h of increase to a pH of  $11.25 \pm 2.27$ , the WPFA reached a cusp. The pH then increased again, reaching  $\text{pH} 12.85 \pm 0.30$  after 24 h (around 2.2 pH units higher than the OPC). The standard deviation was high from the start ( $\sigma_{0\text{h}} = 1.82$ ) until  $t = 4.5$  h, which balanced out over time, reaching  $\sigma_{24\text{h}}$

= 0.30. While the large  $\sigma$  value reflects differences in the absolute value, all three values show the same trend.

## ICP-OES

DW and GW were analysed to determine the leaching of the grout samples (shown in blue in Fig. 2a, b) and will be referred as DW BG or GW BG.

### Ordinary Portland cement

Al, Si and Ti were not measured for all of the aliquots of the OPC samples because of technical difficulties with the ICP-OES. Data without triplicate analyses are indicated by \* in Figure 2. In DW, the leached concentrations of K, Mg and S were below the DW BG (Fig. 2a; see Tables A4 and A6 in Appendix A). The elements with the highest leaching concentrations were Ca, Na and Si, with  $3.46 \pm 3.85$  ppm,  $2.61 \pm 2.80$  ppm and  $1.15 \pm 1.09$  ppm, respectively; showing a strong heterogeneity in leaching behaviour between aliquots from the same sample, even for the unamended cement. Lower concentrations of Al, Fe and Ti (all <1 ppm) were also measured. The highest yields were Na with 1.70%, Si with 0.47% and Ti with 0.12%, while Al, Ca and Fe had % tot. values of approximately 0.01%. In contrast, in GW (Fig. 2b; see Tables A5 and A6 in Appendix A), all elements except Si were below the GW BG, of which Al, Fe and Ti were below the limit of detection (LOD).

The Si concentration was substantially lower ( $0.32 \pm 0.66$  ppm, 0.12% yield).

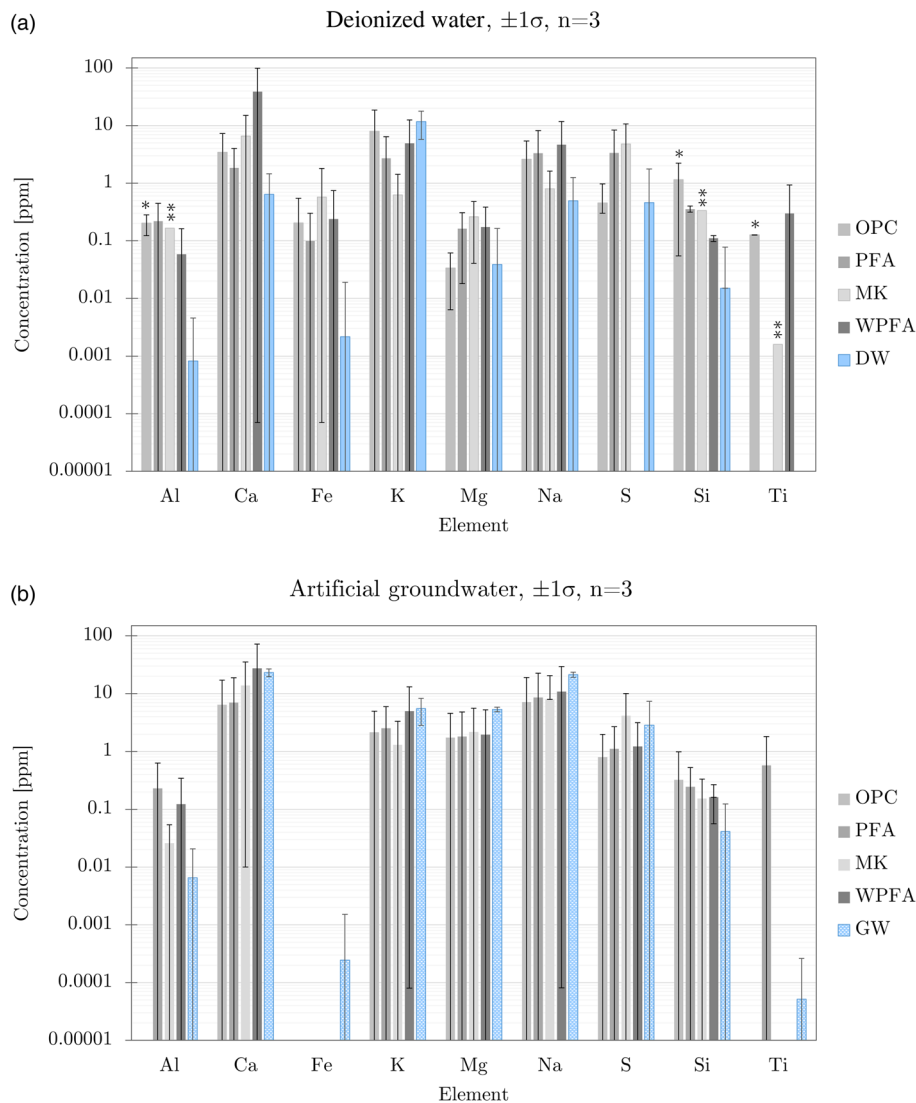
### Pulverized fly ash

In DW, Ca ( $1.85 \pm 2.13$  ppm), Na ( $3.334.85$  ppm) and S ( $3.36 \pm 4.98$  ppm) leached from the PFA sample, with Al, Fe, Mg and Si present only in low concentrations (<0.5 ppm); K was below the DW BG (Fig. 2a; see Tables A4 and A6 in Appendix A) and Ti was below the LOD. In terms of yield, the high Ca concentration still equated to a very low yield (0.01%), with the Na (0.65%), S (0.34%) and Si (0.19%) far more effectively leached. All other extraction yields were negligible. As with the OPC sample, leaching in GW produced much lower yields of the elements, although having larger concentrations leached than in DW (i.e. Ca, Na and S) (Fig. 2b; see Table A5 in Appendix A), and only Al ( $0.23 \pm 0.40$  ppm, negligible yield %), Si ( $0.25 \pm 0.28$  ppm, 0.11%) and Ti ( $0.58 \pm 1.22$  ppm, 0.34%) above the GW BG (see Table A6 in Appendix A). Fe was below the LOD.

### Metakaolin

Al, Si and Ti were not measured for all aliquots of the MK samples because of issues with the ICP-OES. Data without triplicate analyses are indicated by \*\* in Figure 2.

Like the PFA sample, the MK leaching had the highest concentrations for Ca ( $6.64 \pm 8.37$  ppm) and S ( $4.80 \pm 5.83$  ppm),



**Fig. 2.** ICP-OES data (ppm) from grout formulations leached for 24 h in (a) deionized water and (b) artificial groundwater. OPC, ordinary Portland cement; PFA, OPC + pulverized fly ash (1 : 3); MK, OPC + metakaolin (1 : 3); WPFA, OPC + waste paper fly ash (1 : 3). All data are mean and  $1\sigma$  standard deviation ( $n=3$ ), except for \*( $n=2$ ) and \*\*( $n=1$ ) analysis omitted in error in the ICP-OES acquisition program.

although Na, along with Al, Fe, Mg and Si, were present at levels of <1 ppm, and K was below the DW BG (Fig. 2a; see Tables A4 and A6 in Appendix A). These values reflect high percentage yields, with Ca (0.07%), S (1.38%), and Na (0.55%), Fe and Mg (both 0.06%), and Si (0.15%), and with only Al and Ti being negligible. In GW (Fig. 2b; see Tables A5 and A6 in Appendix A) we see the same general reversal, with only Al, Si and S above the GW BG, and even then in very low concentrations (for Al and Si <0.5 ppm), although S was higher at a concentration of  $4.16 \pm 5.89$  ppm (0.42%). Fe and Ti were below the LOD.

### Waste paper fly ash

In sharp contrast to the other samples, the WPFA DW samples had a very high concentration of Ca ( $39.14 \pm 59.70$  ppm, 0.11% yield), high Na ( $4.71 \pm 7.06$  ppm, 1.10%, comparable to the PFA sample), and very low concentrations of Fe, Mg, Si and Ti (<0.5 ppm, all <0.1% yield). K was below the DW BG and Si was below the LOD. Although still substantially reduced, the Ca concentration in GW was still far higher than in any of the other samples ( $27.59 \pm 44.41$  ppm, 0.01%). The other samples showed concentrations of Al ( $0.12 \pm 0.22$  ppm, 0.01%) and Si ( $0.16 \pm 0.11$  ppm, 0.02% yield).

## IC

DW and GW were analysed to determine the leaching of the grout samples (shown in blue in Fig. 3a, b) and will be referred as DW BG and GW BG.

### Ordinary Portland cement

In the OPC sample in DW, the concentrations of numerous anions were below the limit of detection (Fig. 3a; see Table A7 in Appendix A). Except for very low concentrations of  $F^-$  and  $Br^-$  (<0.22 ppm), only  $SO_4^-$  ( $1.21 \pm 1.14$  ppm) and  $Cl^-$  were present in significant quantities ( $96.51 \pm 90.53$  ppm). In GW (Fig. 3; see Table A8 in Appendix A), except for  $NO_2^-$  ( $0.34 \pm 0.26$  ppm),  $Cl^-$  and  $SO_4^-$  were below the DW BG, and all other anions were below the LOD.

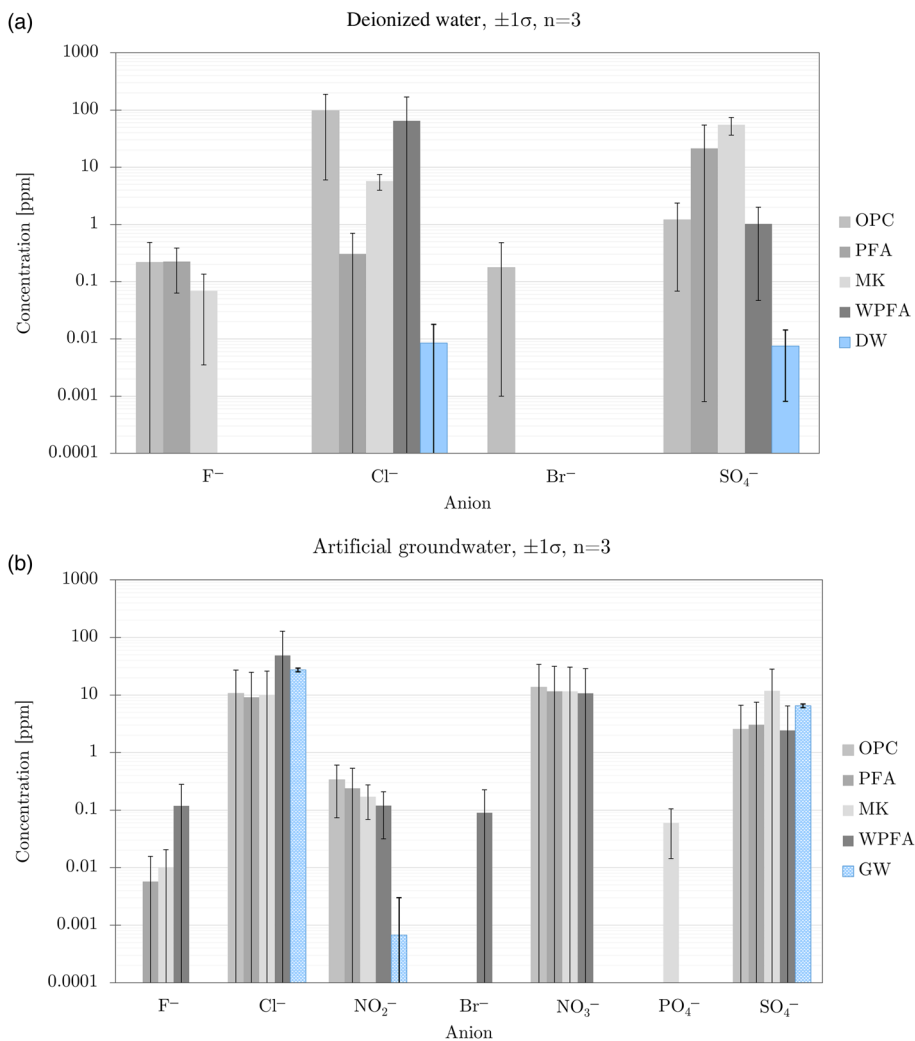
### Pulverized fly ash

In the PFA sample in the DW,  $F^-$  ( $0.23 \pm 0.16$  ppm),  $SO_4^-$  ( $21.29 \pm 33.36$  ppm) and  $Cl^-$  ( $0.30 \pm 0.40$  ppm) were, as in the OPC sample, seen to leach but we observed an order of magnitude more  $SO_4^-$  and an order of magnitude less  $Cl^-$ .  $Br^-$  was below the LOD (Fig. 3a; see Table A7 in Appendix A).

In the GW, we detected that the  $F^-$  concentration was lower ( $0.01 \pm 0.01$  ppm), unlike in the OPC sample, and  $NO_2^-$  ( $0.24 \pm 0.29$  ppm) could be detected, although at lower concentrations than in the OPC (Fig. 3; see Table A8 in Appendix A).

### Metakaolin

The same three anions found in the PFA DW sample were seen in the MK DW sample, although in very different concentrations (Fig. 3a; see Table A7 in Appendix A). In the MK, the  $F^-$  concentration was lower ( $0.07 \pm 0.07$  ppm), while the  $Cl^-$  ( $5.71 \pm 1.76$  ppm) and  $SO_4^-$  ( $55.38 \pm 18.93$  ppm) concentrations were substantially higher. Compared to the OPC,  $F^-$  and  $Cl^-$



**Fig. 3.** IC data (ppm) from grout formulations leached for 24 h in (a) deionized water and (b) artificial groundwater. OPC, ordinary Portland cement; PFA, OPC + pulverized fly ash (1 : 3); MK, OPC + metakaolin (1 : 3); WPFA, OPC + waste paper fly ash (1 : 3). All data are mean and  $1\sigma$  standard deviation ( $n = 3$ ).

concentrations were lower, and the  $\text{SO}_4^-$  concentration was higher, than the values of the OPC. In GW, the MK released  $\text{F}^-$  ( $0.1 \pm 0.01$  ppm) and  $\text{SO}_4^-$  ( $11.80 \pm 16.40$  ppm) at lower concentrations, and we also observed  $\text{NO}_2^-$  ( $0.17 \pm 0.01$  ppm) (Fig. 3; see Table A8 in Appendix A). The MK in GW was the only sample that released  $\text{PO}_4^-$  ( $0.06 \pm 0.05$  ppm).

### Waste paper fly ash

The WPFA DW samples showed even higher  $\text{Cl}^-$  concentrations ( $64.78 \pm 103.30$  ppm) than in the MK and PFA samples (Fig. 3a; see Table A7 in Appendix A). They also had low concentrations of  $\text{SO}_4^-$  (*c.* 1 ppm), and all other anions were below the LOD. In GW, the concentration of  $\text{Cl}^-$  was lower but still substantial ( $48.79 \pm 79.07$  ppm), and this was the only sample to leach  $\text{Cl}^-$  and  $\text{Br}^-$  ( $0.09 \pm 0.13$  ppm) in GW (Fig. 3; see Table A8 in Appendix A). The  $\text{F}^-$  concentration ( $0.012 \pm 0.16$  ppm) in the GW leachate was comparable to that seen in the PFA sample, and we found  $\text{NO}_2^-$  in similar concentrations to all the other GW leaching experiments ( $0.12 \pm 0.09$  ppm).

## Discussion

Our OPC and OPC:SCM samples showed different pH buffer capacities, and these are likely to have been controlled by two factors. The 100% OPC data suggest that one control may be the variability in the OPC mineralogy, which is present despite the use of a single well-homogenized CEM I source. However, the substantial difference between the SCM grout formulations suggests that the SCM mineralogy is likely to be the main factor. Some of the gradient changes in the pH evolutions may suggest that competing or sequential mechanisms are in operation but further high-sensitivity chemical investigations and additional OPC and SCM compositional analysis of the specific aliquots would be needed to confirm this.

From a radioactive waste management perspective, grouts are required to maintain a pH of approximately 11 over a time period of a few thousand years when infiltrated by groundwater (Paulley *et al.* 2020). Our data suggest that the MK sample appears to have equilibrated well within our experimental time for both DW and GW but at a pH well below that required; suggesting that this formulation is less desirable for encapsulation based on pH alone. In contrast, the 100% OPC and WPFA both appear to be evolving to a higher equilibration pH than the currently accepted PFA formulation in both DW and GW during an initial phase of infiltration (as simulated here). The WPFA has already equilibrated to a pH of about 12.5 in GW (slightly higher than the pH of 11 in DW), while the PFA and OPC samples equilibrate at a lower than desired pH in DW, and have not yet reached equilibration in GW (data cannot confirm if they will reach pH *c.* 11). A higher pH value of the WPFA does not impose any issues regarding the waste acceptance criteria, as the required pH of 11 can be maintained (Paulley *et al.* 2020). More work is needed to provide information if the examined SCMs successfully reach a pH of about 11 in the long term.

More nuanced analysis is challenging without homogeneous samples and the ability to measure pH, ICP-OES and IC (ideally with X-ray diffraction (XRD)) simultaneously at each time point, which cannot be achieved on the short timescales and sampling frequency of the equilibration experiments.

When we consider the combined ICP-OES and IC chemical analysis, we see that all elements and anions show high standard deviations for all samples and for both types of water. This indicates a substantial heterogeneity between the three replicates for each sample, as already suggested by the variability in the pH data. It is interesting to note that the heterogeneity in the OPC replicates is as high, if not higher, than that seen in the OPC:SCM samples. The 100% OPC samples did not have the additional challenge of

ensuring a homogeneous SCM distribution during preparation, and all samples were prepared using laboratory standard mixing protocols for homogeneous sample preparation. Despite the homogeneity of the bulk CEM I source, our data suggest that at the scale of each cuboid aliquot, there could be a possible variability in the mineralogy that could affect the element availability, and a probable variability in microcracks and bubble distributions that control the surface area, local water penetration depths and interaction volumes. This is especially probable for short time intervals or when the sample has not reached equilibrium with the water.

Given the heterogeneity of the OPC, the detailed impact and mechanisms of the SCM on leaching is hard to determine with a high degree of confidence, as the relative solubility and accessibility of the different SCM and OPC phases are unknown.

However, DW had lower concentrations of ionic constituents than the GW, and this is reflected in the accelerated leaching (Hartwich and Vollpracht 2017). The chemical data appear to be dominated by the leaching of elements (Ca, Na, S and Si) typically found in the OPC phases such as calcium silicate hydrate (C–S–H), tricalcium silicate ( $\text{C}_3\text{S}$ ) and tetracalcium aluminato ferrite ( $\text{C}_4\text{AF}$ ) (Taylor 1997); however, by mass, the majority of all the leached elements are in the SCM phases. A rapid extraction of the examined elements in DW is visible from the high percentage total (% tot.) values for Na in all of the examined samples, Si in the OPC, PFA and MK, and S in the PFA and MK. A rapid extraction of elements in GW only applies for Si (in the OPC, PFA and MK). Typical for clay (MK) is the dissolution of phyllosilicates, visible as the leaching of Na and Si (García *et al.* 2015). Due to the leaching of Na throughout all samples and Si through most samples, the unique feature of the MK for the dissolution of phyllosilicates cannot be verified within a leaching period of 24 h.

The relatively consistent differences between the leaching in DW and GW found in all of the samples suggest that the ionic equilibrium between the leachant and the samples is critical to leaching. In the more ionic GW, leaching is lower than in the DW with a lower ion concentration, which is almost reached because more elements diffuse in the DW than in the GW. This observation partially agrees with the findings of Hartwich and Vollpracht (2017), which found that alkali (earth) metals (Ba, Ca, Na and K) are leaching without exception in the OPC and PFA. Our study findings only prove the leaching of Na in both samples and higher concentrations of Si ( $>0.25$  ppm) than found in the study of Hartwich and Vollpracht (2017) ( $<0.0001$  ppm). We have shown that the ionic equilibrium cannot be standardized for each element in GW due to a non-consistency in the leached concentration, in addition to the concentrations present in the GW leachant. This agrees with the results of Hartwich and Vollpracht (2017), which found a reduction in the dissolution of ions in cement.

This type of study shows that for the first 24 h, leaching is controlled by diffusion. The dissolution of solid compounds can occur either by diffusion or convection (Ekström 2003). The differences in leaching behaviour between DW and GW and no water flow within the experiment prove the underlying process to be diffusion.

## Conclusions

The results presented in this paper offer an initial assessment of alternative candidates for PFA for use in grout and cement formulations. We show that the leachant composition has a strong influence on leaching behaviour within 24 h of immersion of the grout samples, confirming the general findings of Hartwich and Vollpracht (2017), and that similar behaviour is found in a range of grout formulations (OPC, PFA, MK and WPFA). Based on pH alone, we suggest that the WPFA outperforms OPC and PFA, and

formulations of both, for speed of equilibration and final pH, and that MK also equilibrates rapidly but fails to achieve a high enough pH. All grout formulations achieve a lower final pH value in DW than in GW, suggesting that diffusion is the main control for leaching.

Although challenging to interpret, the elemental and anion analysis suggests that while the WPFA appears a good candidate for LLW encapsulation from the pH data, this sample shows substantial GW leaching of Ca, Na, Cl<sup>-</sup>, Br<sup>-</sup> and NO<sub>2</sub><sup>-</sup>, but a lesser concentration of SO<sub>4</sub><sup>2-</sup>, compared to the other formulations, although these are often close to the PFA formulation data.

Our data suggest that PFA alternatives may be suitable for SCMs for nuclear waste encapsulation, and that a potential suitability can be identified through very rapid equilibration experiments. However, more extensive mineralogical (XRD) and microstructural (SEM and X-ray computerized tomography (XCT)) data before and after leaching are required before the fundamental mechanisms can be identified and the suitability of the SCMs over longer periods confirmed.

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**Author contributions** **AK**: conceptualization (lead), data curation (lead), investigation (lead), methodology (lead), project administration (lead), software (lead), validation (lead), visualization (lead), writing – original draft (lead), writing – review & editing (lead); **TP**: investigation (supporting), resources (supporting); **JCR**: funding acquisition (equal), supervision (equal), writing – review & editing (equal); **KJD**: supervision (equal), validation (equal), writing – review & editing (equal); **FT**: funding acquisition (equal), supervision (supporting), writing – review & editing (equal).

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**Table A1.** Ionic concentration of the artificial groundwater (May et al. 2012)

Ion	Concentration (M)
Ca <sup>2+</sup>	0.0009
Mg <sup>2+</sup>	0.0002
Na <sup>+</sup>	0.0007
K <sup>+</sup>	0.0001
Cl <sup>-</sup>	0.0008
SO <sub>4</sub> <sup>2-</sup>	0.0002
NO <sub>3</sub> <sup>-</sup>	0.0005
HCO <sub>3</sub> <sup>-</sup>	0.0011

**Table A2.** Microwave-assisted extraction (MAE) results per sample

Element	Concentration (ppm)			
	OPC	PFA	MK	WPFA
Al	1836.63 ± 70.66	5256.35 ± 212.34	9552.40 ± 451.13	1766.60 ± 56.00
Ca	37 044.33 ± 1466.85	12 221.00 ± 653.37	8209.30 ± 157.12	33 775.50 ± 1641.19
Fe	1930.13 ± 47.19	3710.85 ± 173.45	302.21 ± 36.56	763.07 ± 28.93
K	342.65 ± 51.69	838.26 ± 54.37	422.46 ± 18.59	418.50 ± 76.15
Mg	1400.30 ± 57.33	1070.41 ± 46.51	370.92 ± 12.76	814.39 ± 39.90
Na	124.80 ± 20.71	436.48 ± 22.56	55.61 ± 6.95	383.24 ± 55.69
S	1201.57 ± 58.10	846.23 ± 42.31	313.56 ± 3.34	1134.40 ± 17.11
Si	239.87 ± 64.01	179.36 ± 22.03	218.85 ± 630.00	589.87 ± 5.37
Ti	101.60 ± 2.63	169.02 ± 8.48	182.71 ± 2.80	329.23 ± 10.42

The examined samples are: OPC, ordinary Portland cement; PFA, pulverized fly ash; MK, metakaolin; WPFA, waste paper fly ash. The errors are provided as 1σ.

**Competing interests** The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

**Data availability** All data generated or analysed during this study are included in this published article (and, if present, its supplementary information files).

## Appendix A

The results from this study are presented in [Tables A1–A8](#).

**Table A3.** ICP-OES analysis of the used deionized water (DW) and artificial groundwater (GW)

Element	Concentration (ppm)	
	DW	GW
Al	0.0008 ± 0.0037	0.0065 ± 0.0140
Ca	0.6409 ± 0.8098	23.3288 ± 3.5999
Fe	0.0022 ± 0.0169	0.002 ± 0.0013
K	11.7971 ± 6.0131	5.5589 ± 2.7337
Mg	0.0387 ± 0.1248	5.3517 ± 2.7337
Na	0.4974 ± 0.7570	21.4297 ± 2.0625
S	0.4606 ± 1.3076	2.8504 ± 4.5271
Si	0.0151 ± 0.0625	0.0413 ± 0.0816
Ti	0	0.0001 ± 0.0002

The errors are provided as 1σ.

**Table A4.** ICP-OES results for grout samples leached for 24 h in deionized water

Element	OPC (100%)			PFA (3 : 1 PFA : OPC)			MK (3 : 1 MK : OPC)			WPFA (3 : 1 WPFA : OPC)		
	C (ppm)	% tot.	% tot.BG	C (ppm)	% tot.	% tot.BG	C (ppm)	% tot.	% tot.BG	C (ppm)	% tot.	% tot.BG
Al	0.2022 ± 0.0793**	0.01	0.01	0.2196 ± 0.2261	0.00	0.00	0.1658*	0.00	0.00	0.0588 ± 0.1038	0.00	0.00
Ca	3.4645 ± 3.8469	0.01	0.01	1.8536 ± 2.1341	0.02	0.01	6.6395 ± 8.3673	0.08	0.07	39.136 ± 59.7004	0.12	0.11
Fe	0.2039 ± 0.3446	0.01	0.01	0.0999 ± 0.2002	0.00	0.00	0.5782 ± 1.2236	0.06	0.06	0.2399 ± 0.5049	0.03	0.03
K	8.0376 ± 10.5203	2.35	0.00	2.7231 ± 3.6813	0.32	0.00	0.6253 ± 0.8008	0.00	0.00	4.9407 ± 7.5539	1.18	0.00
Mg	0.0339 ± 0.0275	0.00	0.00	0.1636 ± 0.1455	0.02	0.01	0.2615 ± 0.2207	0.07	0.06	0.1736 ± 0.2126	0.02	0.02
Na	2.6129 ± 2.7981	2.09	1.70	3.3333 ± 4.8499	0.76	0.65	0.8008 ± 0.8115	1.44	0.55	4.6960 ± 7.0620	1.23	1.10
S	0.4564 ± 0.5143	0.04	0.00	3.3638 ± 4.9758	0.40	0.34	4.8031 ± 5.8319	1.53	1.38	0	0.00	0.00
Si	1.1485 ± 1.0940**	0.48	0.47	0.3563 ± 0.0431	0.20	0.19	0.3348*	0.15	0.15	0.1104 ± 0.013	0.02	0.01
Ti	0.1264 ± 0.0007**	0.12	0.12	0	0.00	0.00	0.0016*	0.00	0.00	0.2997 ± 0.6345	0.09	0.09

The examined samples are: OPC, ordinary Portland cement; PFA, pulverized fly ash; MK, metakaolin; WPFA, waste paper fly ash. The according grout mix ratios are stated in brackets. C, concentration in ppm; % tot., extraction yield of the total; % tot.BG, background correction. The errors are provided as 1 $\sigma$ . \*Only one sample of the triplet was eligible for analysis. \*\*Two samples of the triplet were eligible for analysis.

**Table A5.** ICP-OES results for grout samples leached for 24 h in artificial groundwater

Element	OPC (100%)			PFA (3 : 1 PFA : OPC)			MK (3 : 1 MK : OPC)			WPFA (3 : 1 WPFA : OPC)		
	C (ppm)	% tot.	% tot.BG	C (ppm)	% tot.	% tot.BG	C (ppm)	% tot.	% tot.BG	C (ppm)	% tot.	% tot.BG
Al	0	0.01	0.00	0.2304 ± 0.4010	0.00	0.00	0.0259 ± 0.0278	0.00	0.00	0.1232 ± 0.2186	0.00	0.01
Ca	6.4542 ± 10.6037	0.01	0.00	7.0121 ± 11.8464	0.02	0.00	13.9247 ± 21.2953	0.08	0.00	27.5875 ± 44.411	0.12	0.01
Fe	0	0.01	0.00	0	0.00	0.00	0	0.06	0.00	0	0.03	0.00
K	2.1585 ± 2.7977	2.35	0.00	2.5376 ± 3.4593	0.32	0.00	1.3128 ± 2.0109	0.15	0.00	4.9777 ± 8.2060	1.18	0.00
Mg	1.7356 ± 2.8580	0.00	0.00	1.8100 ± 3.0236	0.02	0.00	2.1833 ± 3.3904	0.07	0.00	1.9564 ± 3.3164	0.02	0.00
Na	7.1846 ± 11.9786	2.09	0.00	8.6343 ± 13.9780	0.76	0.00	7.9793 ± 12.6262	1.44	0.00	10.9251 ± 18.4839	1.23	0.00
S	0.8019 ± 1.1718	0.04	0.00	1.1125 ± 1.5611	0.40	0.00	4.1629 ± 5.8897	1.53	0.42	1.2206 ± 1.9393	0.00	0.00
Si	0.3225 ± 0.6610	0.48	0.12	0.2455 ± 0.2826	0.20	0.11	0.1542 ± 0.1772	0.15	0.05	0.1613 ± 0.1051	0.02	0.02
Ti	0	0.12	0.00	0.5776 ± 1.2244	0.00	0.34	0	0.00	0.00	0	0.09	0.00

The examined samples are: OPC, ordinary Portland cement; PFA, pulverized fly ash; MK, metakaolin; WPFA, waste paper fly ash. The according grout mix ratios are stated in brackets. C, concentration in ppm; % tot., extraction yield of the total; % tot.BG, background correction. The errors are provided as 1 $\sigma$ .



**Table A6.** IC analysis of the deionized water (DW) and artificial groundwater (GW) used

Ion	Concentration (ppm)	
	DW	GW
F <sup>-</sup>	0	0
Cl <sup>-</sup>	0.0084 ± 0.0095	27.2320 ± 2.0322
NO <sub>2</sub> <sup>-</sup>	0	0.007 ± 0.0023
Br <sup>-</sup>	0	0
NO <sub>3</sub> <sup>-</sup>	0	0
PO <sub>4</sub> <sup>-</sup>	0	0
SO <sub>4</sub> <sup>-</sup>	0.0075 ± 0.0067	6.5098 ± 0.4767

The errors are provided as 1 $\sigma$ .

**Table A7.** IC results of grout samples leached for 24 h in deionized water

Ion	Concentration (ppm)			
	OPC (100%)	PFA (3 : 1 PFA : OPC)	MK (3 : 1 MK : OPC)	WPFA (3 : 1 WPFA : OPC)
F <sup>-</sup>	0.2171 ± 0.2699	0.2252 ± 0.1621	0.0693 ± 0.0658	0
Cl <sup>-</sup>	96.5117 ± 90.5255	0.3048 ± 0.3955	5.7117 ± 1.7588	64.7761 ± 103.3038
NO <sub>2</sub> <sup>-</sup>	0	0	0	0
Br <sup>-</sup>	0.1760 ± 0.3048	0	0	0
NO <sub>3</sub> <sup>-</sup>	0	0	0	0
PO <sub>4</sub> <sup>-</sup>	0	0	0	0
SO <sub>4</sub> <sup>-</sup>	1.2105 ± 1.1422	21.2868 ± 33.3604	55.3807 ± 18.9277	1.0202 ± 0.9734

The examined samples are: OPC, ordinary Portland cement; PFA, pulverized fly ash; MK, metakaolin; WPFA, waste paper fly ash. The according grout mix ratios are stated in brackets. The errors are provided as 1 $\sigma$ .

**Table A8.** IC results of grout samples leached for 24 h in artificial groundwater

Ion	Concentration (ppm)			
	OPC (100%)	PFA (3 : 1 PFA : OPC)	MK (3 : 1 MK : OPC)	WPFA (3 : 1 WPFA : OPC)
F <sup>-</sup>	0	0.0057 ± 0.0099	0.0102 ± 0.0103	0.1191 ± 0.1599
Cl <sup>-</sup>	10.6862 ± 16.4898	9.19332 ± 15.5334	9.8733 ± 16.1062	48.7917 ± 79.0718
NO <sub>2</sub> <sup>-</sup>	0.377 ± 0.2645	0.2391 ± 0.2915	0.1714 ± 0.1029	0.1195 ± 0.0878
Br <sup>-</sup>	0	0	0	0.0901 ± 0.1338
NO <sub>3</sub> <sup>-</sup>	13.6759 ± 20.4555	11.6479 ± 19.6264	11.6501 ± 18.7904	10.7610 ± 18.0914
PO <sub>4</sub> <sup>-</sup>	0	0	0.0596 ± 0.0453	0
SO <sub>4</sub> <sup>-</sup>	2.5408 ± 4.0733	3.0563 ± 4.4317	11.8040 ± 16.4011	2.4402 ± 4.0030

the errors are provided as one sigma.

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