

Immobilization of arsenate and fluoride from alkaline industrial wastes via induced hydrotalcite and brucite formation: Implications for the solidification of radioactive waste

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ABSTRACT

Coal fly ash and granulated blast furnace slag (GBFS) can potentially be utilized as highly effective binders for the solidification and stabilization of radioactive waste. This study investigated a novel immobilization strategy by inducing the formation of magnesium-bearing minerals, specifically hydrotalcite and brucite, through the addition of magnesium oxide (MgO) and magnesium nitrate [Mg (NO₃)₂]. Mineralogical transformations were monitored over two weeks with varying Mg-source ratios (10%–30%). Results showed that MgO addition successfully induced stable hydrotalcite and brucite phases, significantly enhancing fluoride removal in GBFS from 53% to over 97%. In contrast, Mg nitrate led to pH reduction and the formation of less stable hydrocalumite. Selective dissolution and leaching tests confirmed that anions co-precipitated with hydrotalcite remained sequestered at pH as low as 5.6, whereas calcium-bearing minerals dissolved at pH 9, releasing sorbed anions. These findings demonstrate that controlling pore-water chemistry through slightly soluble MgO provides a possible long-term sequestration mechanism for arsenate and fluoride as analogues of highly mobile radioactive oxyanions, highlighting the potential of industrial by-product-based binders for radioactive waste solidification applications.

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INTRODUCTION

The safe containment of radioactive material remains an urgent global challenge because the world currently has over 37 million cubic meters of radioactive waste requiring long-term management (International Atomic Energy Agency [IAEA], 2022). Low-level radioactive waste accounts for more than 90 percent of this total volume (IAEA, 2022), presenting specific containment issues due to highly mobile and volatile anionic radionuclides. For instance, radioactive selenate (SeO₄²⁻) and iodine ions (I⁻) and (IO₃⁻) possess exceptionally low sorption affinities to traditional barrier surfaces, leading to rapid leaching into subsurface environments (Machesky et al., 2021; Um et al., 2022). Traditional solidification methods can sometimes fail under aggressive environmental conditions, as conventional Portland cement lacks the specialized structural sites needed to chemically bond these highly soluble species (Li & Chen, 2021). Modern remediation strategies now explore using alkaline industrial byproducts like iron slag and coal fly ash to build stable binder matrices (Shi & Day, 2026). These systems create robust crystalline networks such as calcium-silicate-hydrate (C-S-H) gels and structural ettringite phases that physically encapsulate and chemically capture these elusive contaminants (Macha et al., 2020). Understanding these specific hydration pathways provides critical design implications for the permanent solidification of low-level nuclear waste.

KEYWORDS

Arsenate, Brucite, Coal fly ash, Fluoride, Granulated blast furnace slag, Hydrotalcite, Radionuclide sequestration, Solidification/Stabilization

This remediation strategy simultaneously addresses broader industrial sustainability because iron slag and coal fly ash are increasingly recycled as cement aggregates to promote zero emissions (Bielecka & Kulczycka, 2020). Currently, the global recycling rate for iron slag stands at approximately 50–66%, largely due to its established utility in road bases, asphalt mixtures, and structural fills (World Steel Association, 2021). In contrast, the global utilization rate of coal fly ash remains disproportionately low at around 40%, despite its well-documented pozzolanic value (Wang et al., 2023). Consequently, millions of tons of these by-products are still disposed of in landfills and ash ponds, thereby neglecting their economic potential and an ongoing environmental liability (Dhoble and Ahmed, 2021; Yao et al., 2015).

Supplementary cementitious materials like coal fly ash and steel slag work effectively in the solidification and stabilization of radioactive waste (Ojovan & Lee, 2014). These materials enhance traditional Portland cement matrices by refining pore structures through secondary pozzolanic reactions. Reactive silica and alumina in coal fly ash combine with calcium hydroxide to generate additional calcium silicate hydrate gel (Glasser, 1992). This secondary gel fills microscopic voids to drastically reduce overall permeability. The mineral framework then physically locks migrating radioactive isotopes within the matrix. Incorporating iron slag like ground granulated blast furnace slag also provides a crucial reductive environment driven by inherent reduced sulfur species. This chemical mechanism lowers the oxidation state of highly mobile radionuclides to prevent groundwater leaching (Lukens et al., 2005). The process reduces soluble pertechnetate into insoluble technetium and converts hexavalent chromium into stable trivalent chromium. Blending these materials aids in critical thermal management by lowering the exothermic heat of hydration generated by pure clinker. This thermal control mitigates thermal gradients and micro-cracking to ensure the long-term structural integrity of large-scale waste blocks and deep geologic canisters (Mindess et al., 2003).

However, the weathering of cement-based matrices containing steel slag and coal fly ash for radioactive waste disposal drives the transformation of metastable primary phases into thermodynamically stable secondary minerals. Initially, the hydration and hydrolysis of metal oxides (primarily CaO) generate a hyperalkaline pore fluid (pH ~11). This promotes the rapid precipitation of Ca-bearing minerals like portlandite, ettringite, and calcium silicate hydrates (C-S-H) (Lothenbach et al., 2011). Under these high-pH conditions, the glassy ash surfaces dissolve, releasing ions and potentially mobilizing toxic trace elements as soluble anionic species. As the fluid supersaturates, amorphous aluminosilicate crusts form on the particle surfaces (Provis & Bernal, 2014). Over time, carbonation and ongoing precipitation reactions buffer the pore water to circum-neutral levels (pH ~8). This pH drop limits further rapid dissolution, and the system gradually ages, converting the initial amorphous gels into stable crystalline phases such as iron oxides, clay minerals, and zeolites, which can permanently sequester residual contaminants (Ochs et al., 2016).

While surface adsorption and solid-solution formation can effectively reduce dissolved ion concentrations below pure-phase saturation levels, oxyanionic radionuclides present a unique challenge. During the weathering of cement-based matrices, mobile oxyanions—such as selenate (SeO_4) and iodate (IO_3) often remain highly concentrated and active at the near-neutral to high pH levels typical of most hydrogeological environments. This extreme mobility occurs because very few secondary minerals develop a permanent positive charge under these alkaline conditions; instead, their pH-dependent surface charges are predominantly negative, creating an electrostatic barrier that

naturally repels these specific anions (Cornelis et al., 2008; Ochs et al., 2016). Consequently, the long-term immobilization of highly soluble species like radioactive selenate and oxidized iodine remains one of the most difficult variables to control in the solidification and stabilization of radioactive waste (Guo et al., 2017).

Recent studies on weathered alkaline matrices demonstrate that conventional secondary minerals fail to control oxyanion partitioning at high pH (Cornelis et al., 2008; Ochs et al., 2016). Amorphous iron and aluminum oxides also do not act as stable sinks because they electrostatically repel oxyanions at extreme alkalinity and lose their limited sorption capacity as they age. However, recent advancements in alternative cementitious waste forms have identified magnesium-bearing minerals like hydrotalcite and magnesium silicate hydrates as highly effective sorbents. Incorporating reactive magnesia or calcined hydrotalcite into engineered binders successfully immobilizes difficult radioactive oxyanions via structural incorporation and strong electrostatic capture under highly alkaline conditions (Marsiske et al., 2021; Tian et al., 2020; Wang et al., 2024). While conventional hydrotalcite retention relies on weak and highly reversible anion-exchange reactions, natural geological analogues demonstrate that these minerals can achieve stable and irreversible incorporation of aqueous anions when forming in tandem with magnesium-rich phases (Chavagnac et al., 2013). This permanent retention is fundamentally controlled by the magnesium-to-aluminum ratio which directly dictates layer charge density and interlayer spacing (Opiso et al., 2010; Liu et al., 2013). Decreasing the magnesium-to-aluminum ratio increases the positive charge density of the basal layers to transition the mineral from a weak anion-exchanger to a highly selective trap that binds oxyanions via strong electrostatic and inner-sphere complexation (Jung et al., 2021; Yamasaki et al., 2023). Therefore, strategically controlling this ratio in engineered hydrotalcite phases presents a highly viable pathway to decrease anion exchangeability and permanently encapsulate radioactive oxyanions.

This study evaluates the potential valorization of iron slag and coal fly ash as cementitious binders for radioactive waste stabilization. The primary focus centers on controlling hydrotalcite formation to permanently immobilize arsenate and fluoride. Actual radioactive nuclides are exceptionally difficult to handle in standard experimental environments due to severe radiation safety hazards and strict regulatory restrictions. Therefore, this research utilizes arsenate and fluoride as safe non-radioactive chemical and structural analogues to simulate the behavior of highly mobile radioactive oxyanions like selenium or iodine isotopes. To achieve this objective the study formulates an ideal blending ratio of iron slag and coal fly ash supplemented with magnesium oxide and magnesium nitrate. This formulation systematically controls the magnesium-to-aluminum ratio to optimize the precipitation of

hydrotalcite-like layered double hydroxides during hydration. The non-radioactive analogues are thoroughly incorporated into the engineered matrices prior to curing. Lastly standardized and accelerated leaching tests determine the immobilization efficiency of the hydrated samples by measuring the precise release rates of fluoride under simulated environmental weathering and varying pH conditions.

MATERIALS AND METHODS

Materials

The primary alkaline waste materials used were CFA and GBFS collected from power and iron smelting companies in Japan. The major components of CFA (in weight percentage of oxides) are CaO (50.10%), SiO2 (23.09%), Al2O3 (21.38%), MgO (3.45%) and Fe2O3 (1.04%). The main mineral compositions of CFA as shown in Fig.1 include amorphous materials as suggested by a broad background peak around the diffraction area of 27 to 30 o2θ, calcite (CaCO3), magnesite (MgCO3), carbonate-fluorapatite (Ca10(PO4)5CO3F1.5(OH)0.5) and gehlenite (Ca2Al2SiO7).

The steel slag used in this study is a granulated blast furnace slag (GBFS) collected from an iron smelting company in Japan. The major components of GBFS (in weight percentage of oxides) are CaO (43.77%), SiO2 (32.30%), Al2O3 (13.75%), MgO (6.49%) and Fe2O3 (0.35%). Although GBFS has similar chemical composition to CFA of which the total amount of CaO and SiO2 accounts for more than 70% and the MgO content is very low, the mineral composition of GBFS is different from CFA and it is mainly composed of amorphous materials as shown in Figure 1.

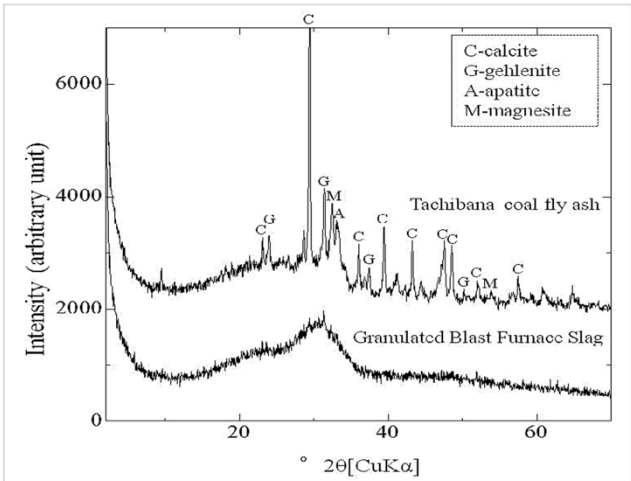


Figure 1: Mineralogical compositions of T-CFA and GBFS reflected by X-ray diffractograms.

Since the Mg content is a significant consideration in the formation of the Mg-containing minerals, different ratios of MgO and Mg nitrate to CFA and GBFS were prepared for the hydration experiments. To induce mineral formation, slightly soluble periclase (MgO) and highly soluble magnesium nitrate were utilized. The chemical formula for Mg nitrate used here is Mg (NO3)2·6H2O.

Hydration Experiments

To compare the effect of Mg concentration on hydration products, different ratios of Tachibana coal fly ash (T-CFA) to MgO and Mg nitrate respectively, and different ratios of GBFS to MgO and Mg nitrate respectively were prepared for hydration experiments to control secondary formation of Mg-containing minerals.

Table 1: Chemical Conditions of Hydration Experiments for T-CFA and GBFS

Sample Series	Sample Name	T-CFA (g)	GBFS (g)	MgO (g)	Mg Nitrate (g)	H2O (mL)	Duration Week
GBFS (SL Series)	SL-1 to SL-4	0	10→7	0→3	0	40	1
	SL-5 to SL-8	0	10→7	0→3	0	40	2
	SL-9 to SL-12	0	9.0→7.5	0	1.0→2.5	40	1
	FA-1 to FA-4	10→7	0	0→3	0	40	1
T-CFA (FA Series)	FA-5 to FA-8	10→7	0	0→3	0	40	2
	FA-9 to FA-12	9.0→7.5	0	0	1.0→2.5	40	1
	FA-13 to FA-16	9.0→7.5	0	0	1.0→2.5	40	2

Note: The arrow symbol → signifies a step-wise alteration across the incremental sample ranges (e.g., base material decreases incrementally by 1.0 g or 0.5 g steps as additive loading increases by corresponding step amounts).

Table 1 summarizes the compressed chemical formulations and step-wise loading parameters of these prepared samples. The ratio of liquid to solid was 4 (40ml/10g). The effect of hydration time was also examined to confirm the stability of secondary minerals as the hydration reaction proceeds with time. To accelerate hydration reaction, the samples were hydrated using deionized (DI) water at a temperature of 50°C for 1 or 2 weeks. The reacted samples were then collected by centrifugation at 3000 rpm for 40 minutes and freeze dried prior to analysis. The dried solid samples were analyzed by XRD to determine the chemical and mineralogical transformation.

Sorption Experiments

Fluoride sorption experiments

The stock solutions for fluoride sorption experiments were prepared by dissolving a specified quantity of sodium fluoride (NaF) in deionized water to achieve an initial fluoride concentration of 100 ppm. Fluoride sorption assays utilizing granulated blast furnace slag (GBFS) with magnesium nitrate additions were omitted, as the resulting hydration products remained predominantly amorphous. Table 2 summarizes the chemical conditions and step-wise blending parameters of the prepared sorption runs for Tachibana coal fly ash (T-CFA) and the GBFS (SL) series.

Table 2: Chemical Conditions of Fluoride Sorption Experiments for T-CFA and GBFS

Sample Series	Sample Name	T-CFA (g)	GBFS (g)	MgO (g)	Mg Nitrate (g)	H ₂ O (mL)	Duration Week
GBFS (SG Series)	SL-F-1 to SL-F-4	0	10→7	0→3	0	40	1
	SL-F-5 to SL-F-8	0	10→7	0→3	0	40	2
	FA-F-1 to FA-F-4	10 →7	0	0→3	0	40	1
T-CFA (FA Series)	FA-F-5 to FA-F-8	10 →7	0	0→3	0	40	2
	FA-F-9 to FA-F-12	9.0→7.5	0	0	1.0 →2.5	40	1
	FA-F-13 to FA-F-16	9.0→7.5	0	0	1.0 →2.5	40	2

Note: The initial concentration of fluoride in the NaF solution is fixed at 100 ppm across all sorption mixtures. The arrow symbol → signifies a step-wise alteration across the incremental sample range

For each individual experimental run, a 10 g fraction of the dry composite mixture was reacted with 40 mL of the 100-ppm NaF stock solution. Following continuous contact for either 1 or 2 weeks at a controlled temperature of 50°C, the reacted solids were isolated via centrifugation at 3000 rpm for 40 minutes and freeze-dried to check the structural transformations. We subsequently evaluated the dry solid residues using X-ray diffraction (XRD) to evaluate post-sorption phase changes, while the remaining equilibrium fluoride concentration in the collected supernatant fluids was verified quantitatively through ion chromatography (IC).

Arsenate sorption experiments

The stock solutions for arsenate sorption experiments were made by dissolving appropriate amounts of sodium arsenate (Na₂HAsO₄·7H₂O) in deionized water. Original concentrations of both 10 and 100 ppm were used in the sorption experiments. The samples for the sorption experiments were prepared in 10 ppm and 100 ppm concentration as shown in Table 3.

Table 3: Chemical Conditions of Arsenic (As) Sorption Experiments for T-CFA

Sample Name	T-CFA (g)	MgO (g)	H ₂ O (mL)	Initial As Concentration (ppm)	Duration Week
FA-As10-1 to FA-As10-3	10 → 7.5	1.0 → 2.5	40	10	1
FA-As10-4 to FA-As10-6	10 → 7.5	1.0 → 2.5	40	10	2
FA-As100-1 to FA-As100-3	10 → 7.5	1.0 → 2.5	40	100	1
FA-As100-4 to FA-As100-6	10 → 7.5	1.0 → 2.5	40	100	2

Note: The arrow symbol → signifies a systematic step-wise alteration across the incremental sample series configurations.

After reacting for one or two weeks at a temperature of 50 °C, the solids were then collected by centrifugation at 3000 rpm for 40 minutes and freeze dried prior to analysis. The dried solid samples were analyzed by XRD to determine the mineralogical transformation after hydration while the supernatant was analyzed for remaining arsenate concentrations by using ICP-AES.

Leaching Test

To evaluate the anion sorption capacity of hydrotalcite, selective dissolution of the Ca-containing minerals from the fluoride-laden samples after sorption experiments for two weeks was performed by controlling leaching pH using the auto-titration machine. The pH was set to 9, 7, 5.6, and adjusted by 1 M nitric acid. The dissolution reactions were allowed for 4 hours. Compared with the pH effect on fluoride leaching, water-based leaching on these samples was also conducted. Moreover, desorption tests on samples after sorption experiments for one and two weeks were conducted to check whether the existence of competitive anion could lead to the release of anion. 0.1M NH₄Cl, 0.1M KCl, and 0.01 M KCl solutions were used for fluoride desorption. After the leaching tests, the concentrations of leached fluoride were measured by using IC. The mineral transformation after selective dissolution was investigated by XRD.

RESULTS AND DISCUSSION

Mineralogical Transformation during hydration

Without MgO and Mg nitrate addition

The hydration of CFA resulted in a significant mineralogical transformation from the original phases as shown in Figure 2. The disappearance of magnesite and carbonate-fluorapatite lead to the formation of ferrian sepiolite (Mg,Fe)₄Si₆O₁₅(OH)₂₆H₂O, akermanite (Ca₂MgSi₂O₇) and hydrocalumite (Ca₄Al₂(OH)₂₆H₂O). The mineral calcite showed increased peak intensity after hydration, indicating their favorable formation. Moreover, the hydration time after one and two weeks showed similar characteristics in terms of mineralogical composition. However, the hydration of GBFS showed no significant difference in mineralogy except for the broadening of the amorphous peak around 20 to 25 °2θ after two weeks of hydration time which could be attributed to the precipitation of amorphous Si and aluminosilicate phase.

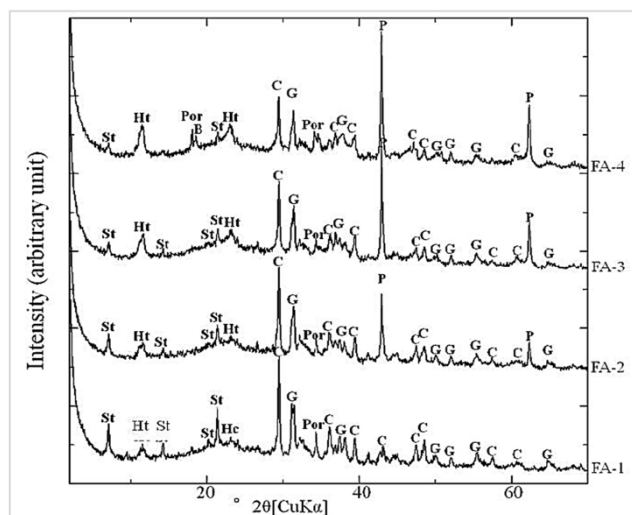


Figure 2: X-ray diffractograms of T-CFA with different ratios of MgO after hydration for one week (Note: St-stilpnomelane; Hc-hydrocalumite; C-calcite; G-gehlenite; Por-portlandite; Ht-hydrotalcite; B-brucite; P-periclase)

With MgO and Mg nitrate addition

The addition MgO greatly changed the mineralogy of CFA after hydration as shown in Figure 3 below. The presence of well-ordered hydrotalcite peak around 7.6 Å confirmed that by controlling the pore water chemistry of CFA during hydration, the secondary formation of this mineral phase can occur. As the hydration time increases, the intensity of hydrotalcite peak in ST-04 samples also increases. The occurrence of hydrocalumite in ST-03 samples was only observed during the first week as evident by the presence of a branched peak around 7.6 Å. It can be observed also that the secondary formation of sepiolite was not observed compared to the hydration of CFA samples without MgO. Moreover, the amount of calcite decreased significantly with time in contrast to the pure CFA and replaced by the formation of portlandite (Ca(OH)₂). Brucite was also observed in addition to periclase which was the source of Mg.

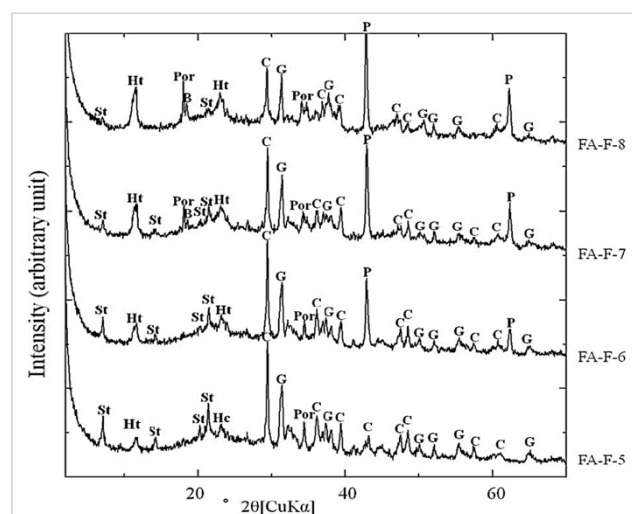


Figure 3: X-ray diffractograms of T-CFA with different ratios of MgO after hydration for two weeks (Note: St-stilpnomelane; Hc-hydrocalumite; C-calcite; G-gehlenite; Por-portlandite; Ht-hydrotalcite; B-brucite; P-periclase)

The addition of MgO to GBFS samples (see Figure 3) also resulted in the secondary formation of hydrotalcite phases but with lower peak intensity compared to CFA samples with MgO. This could

probably be attributed to the favorable formation of brucite which resulted into lesser amount of Mg necessary for favorable hydrotalcite precipitation. Moreover, as the hydration reaction proceeds, the peak of hydrotalcite decreased together with periclase but the brucite peak increased. The favorable formation of brucite as the hydration reaction proceeds could be directly related to the higher Mg content of GBFS which were liberated as hydration proceeds and the lower L/S ratio used compared to CFA. Hence, the need to lower the MgO ratio in GBFS must be considered in order to have the favorable generation of hydrotalcite phases. Moreover, calcite was also observed after hydration regardless of reaction time.

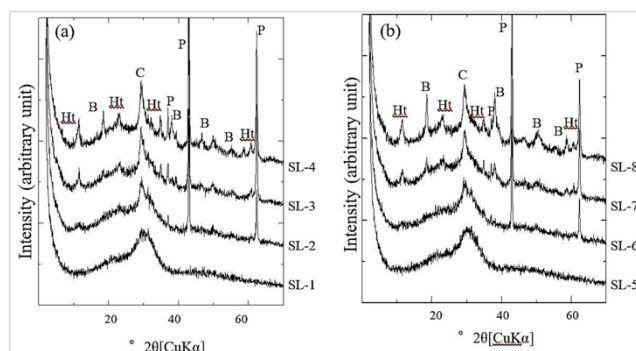


Figure 4: X-ray diffractograms of GBFS with different ratios of MgO after hydration for one (a) and two weeks (b) (Note: Ht-hydrotalcite; B-brucite; C-calcite; P-periclase)

The hydration products of GBFS (SL-1) shown in Figure 4a were amorphous materials, showing no significant difference in mineralogy compared to its original phases. With 10% MgO addition in SL-2, the newly precipitated phase was calcite, while periclase peaks observed in XRD patterns were ascribed to undissolved MgO. Further increases in MgO addition greatly altered the hydration products. In SL-3 and SL-4, the generated mineral phases included hydrotalcite, brucite and calcite. Particularly in SL-4 with 30% MgO addition, the peak intensity of brucite and hydrotalcite was greatly increased. The hydration products of GBFS without or with MgO addition after two weeks (in Figure 4b) were of similar XRD patterns to those after one week. More brucite was precipitated in SL-8 than in SL-4.

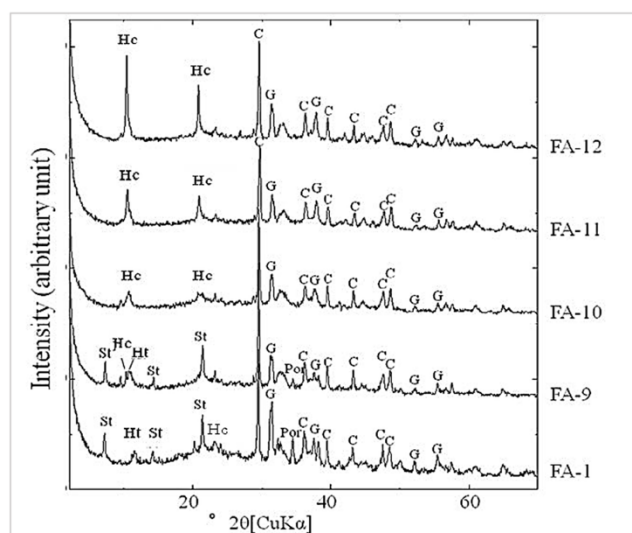


Figure 5: X-ray diffractograms of T-CFA with different ratios of Mg nitrate after hydration for one week (Note: St-stilpnomelane; Ht-hydrotalcite; Hc-hydrocalumite; C-calcite; G-gehlenite; Por-portlandite)

On the other hand, the addition of Mg nitrate to CFA also resulted in significant mineralogical transformation after hydration for one week as shown in Figure 5. In FA-9, into which 10% Mg nitrate was added, mineral phases such as hydrotalcite, portlandite, hydrocalumite and stilpnomelane were precipitated. The primary minerals such as magnesite and carbonate-fluorapatite in CFA also disappeared while calcite and gehlenite phases were preserved after hydration. Compared to FA-1 with no Mg source addition, the intensity of portlandite, gehlenite, and stilpnomelane peaks decreased while the intensity of hydrocalumite and calcite seemed to increase in FA-9 with 10% Mg nitrate addition. Further increases in Mg nitrate addition (FA-10, FA-11, FA-12) didn't result in the appearance of stilpnomelane, hydrotalcite and portlandite while the precipitation of hydrocalumite increased corresponding to Mg nitrate addition. After hydration for 2 weeks (see Figure 6), the hydration products of CFA with Mg nitrate addition showed similar XRD patterns to those after hydration for one week. In the case of GBFS, the addition of Mg nitrate performed no influence on the hydration products which were mainly amorphous regardless of hydration time.

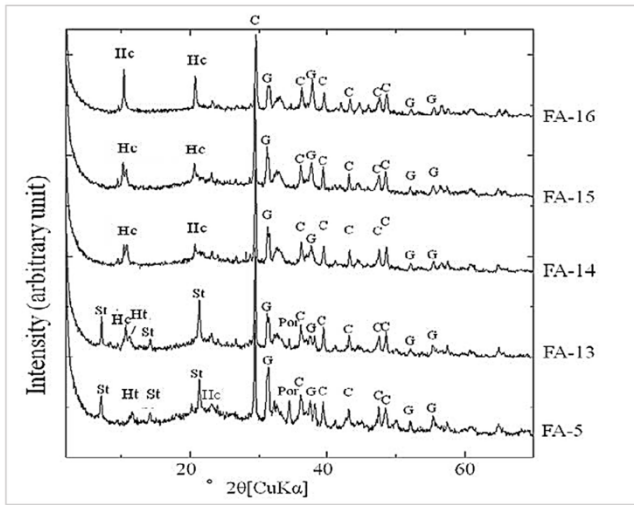


Figure 6: X-ray diffractograms of T-CFA with different ratios of Mg nitrate after hydration for two weeks (Note: St-stilpnomelane; Ht-hydrotalcite; Hc-hydrocalumite; C-calcite; G-gehlenite; Por-portlandite)

Table 4: Remaining concentrations of Arsenic (As) and the final pH in solution after sorption experiments using T-CFA with different ratios of Mg nitrate

Samples	Final pH	Final concentration (ppm)	Sample	Final pH	Final concentration (ppm)
FA-As10-1	12.10	0.003	FA-As100-1	12.15	0.13
FA-As10-2	11.10	0.004	FA-As100-2	11.48	0.006
FA-As10-3	10.50	0.003	FA-As100-3	11.02	0.016
FA-As10-4	11.92	0.003	FA-As100-4	11.95	0.009
FA-As10-5	10.46	0.002	FA-As100-5	11.93	0.006
FA-As10-6	10.89	0.003	FA-As100-6	11.05	0.019

Note: The initial concentration of fluoride in the NaF solution is fixed at 100 ppm across all sorption mixtures. The arrow symbol → signifies a step-wise alteration across the incremental sample ranges.

The hydrocalumite peak also in ST-08 increased in intensity compared to hydrotalcite which the exact opposite to ST-04 in which hydrotalcite peak was higher than hydrocalumite. This result might be attributed to mineral solubility of portlandite and hydrocalumite which control the Ca concentration. In the presence of high arsenic concentration of 100 ppm, the generation of hydrocalumite peak after two weeks in ST-10 samples was not observed. Moreover, the hydrocalumite peak was more evident compared to hydrotalcite in ST-11 and ST-12 samples which contained less amount of MgO (only 10% by weight). Sepiolite was also observed in addition to calcite and periclase.

Sorption of Arsenate and Fluoride during Hydration of CFA and GBFS

Sorption of Arsenate after hydration

The uptake of arsenate after hydration of TFA and GBFS with or without MgO addition was very high in which all the arsenate concentration in the leachates of the hydrated samples were below the detection limit of ICP-AES. This result is expected since the mineral phases generated have high arsenate affinity. It has been proven in literature that not only hydrotalcite and brucite have high uptake capacity of arsenate at hyperalkaline condition but also hydrocalumite, calcite and portlandite. However, these Ca-bearing minerals are stable only under hyperalkaline conditions (Cornelis et al., 2008). Table 3 shows the summary of the leachate pH and the observed mineralogy of all samples with/without MgO addition after hydration in the presence/absence of arsenate. In the case of GBFS, the presence of 729 ppm Mg concentration (adjusted based on the results of dissolved Mg concentration during flow-through experiments) was not enough to generate hydrotalcite phases after hydration and the samples of SG-05 to SG-08 were still largely dominated by amorphous phases. In the absence of arsenate (and SG-06), small amount of calcite was observed after one week in SG-05 while only hydrocalumite was detected after the succeeding week for SG-06. These two secondary mineral phases were not observed in the presence of arsenate which may suggest that arsenate can strongly inhibit their precipitation in these systems. Moreover, the XRD profiles for GBFS and MgO mixtures of SG-09 and SG-10 showed similar characteristics with SG-03 and SG-04, respectively.

In the case of TFA, the hydration of ST-05 and ST-06 in the presence of arsenate but without MgO addition showed similar XRD pattern with ST-01 and ST-02 which indicate that the presence of arsenate does not inhibit their formation during hydration. In ST-07 and ST-08 which was hydrated in the presence of arsenate and contained 30% of MgO by weight, their mineralogical composition slightly varies with ST-03 and ST-04 which have the same GBFS and MgO blend ratio.

Although the peak intensity may vary slightly after different anion sorption, the mineralogical compositions are the same as their hydration products in the absence of anions. Their XRD patterns are not shown here. With respect to their arsenate removal efficiency, it was found that the samples of T-CFA with and without Mg nitrate addition showed extremely high anion removal efficiency (ranging from 98 to 100%), with sorption duration (1 and 2 weeks) and original anion concentration (10 and 100 ppm). The remaining concentrations of As in solution after sorption experiments are listed in Table 4. In the case of arsenate sorption, the arsenic concentration was reduced from 10 ppm to a safe range

of 0.002 to 0.004 ppm by the samples of T-CFA with or without Mg nitrate addition after sorption for one and two weeks; and from 100 ppm to a range of 0.006 to 0.019. Based on the sorption results, the addition of Mg nitrate into T-CFA didn't show significant influence on arsenate sorption.

Sorption of Fluoride after hydration

Figure 7 presents the XRD patterns of the samples after fluoride sorption for one week. The hydration products of the samples in the presence of fluoride showed almost similar XRD patterns to those of the same T-CFA to MgO ratio in the absence of fluoride. However, the intensity of hydrotalcite and portlandite peaks increased slightly in the presence of fluoride compared to those in the absence of fluoride. In addition, particular in FA-F-3 brucite which didn't appear in FA-3 was observed, and the intensity of brucite peak increased in FA-F-4 in comparison to FA-4. Figure 8 shows the XRD patterns of the samples after fluoride sorption for two weeks.

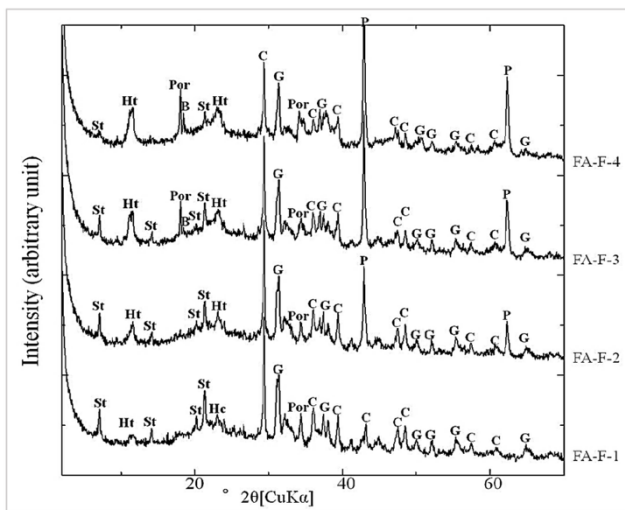


Figure 7: X-ray diffractograms of T-CFA with different ratios of MgO after fluoride sorption for one week (Note: St-stilpnomelane; Hc-hydrocalumite; C-calcite; G-gehlenite; Por-portlandite; Ht-hydrotalcite; B-brucite; P-periclase)

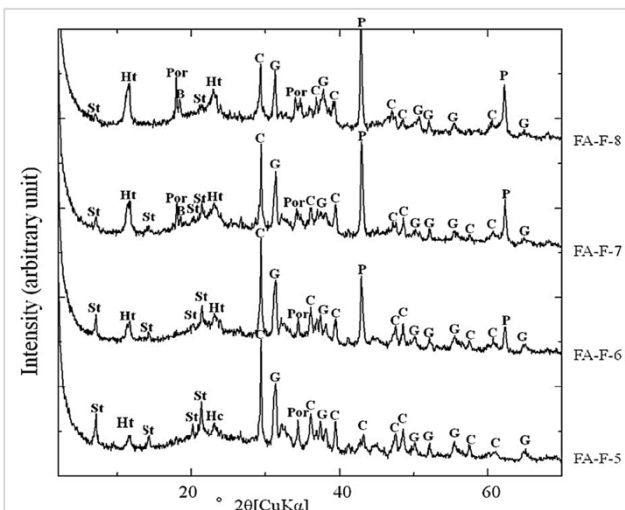


Figure 8: X-ray diffractograms of T-CFA with different ratios of MgO after fluoride sorption for two weeks (Note: St-stilpnomelane; Hc-hydrocalumite; C-calcite; G-gehlenite; Por-portlandite; Ht-hydrotalcite; B-brucite; P-periclase)

Compared to those after fluoride sorption for only one week, they precipitated relatively more hydrotalcite and brucite while the amount of portlandite decreased slightly.

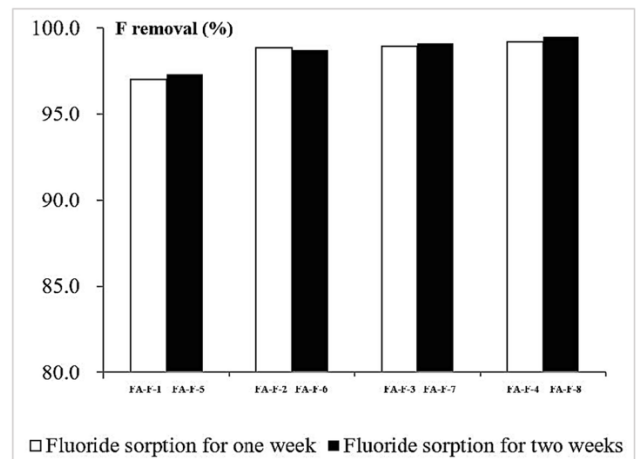


Figure 9: Fluoride removal efficiency of T-CFA with addition of different ratios of MgO after fluoride sorption for one and two weeks.

Fluoride removal efficiency refers to the percentage of fluoride removed from the fluoride solution by the samples of different ratios of T-CFA to MgO, and it is presented in Figure 9. The removal efficiency of T-CFA (FA-F-1 and FA-F-5) used in this study was very high, about 97% of fluoride was removed. With increases of MgO percentage in T-CFA, only slight increases in fluoride sorption were observed after fluoride sorption experiments for one and two weeks. It is clear that the effect of reaction time (one and two weeks) on fluoride removal was insignificant. However, it is worth noting that the remaining fluoride concentration in the solution (FA-F-8) was reduced to 0.5 ppm, lower than the Japanese water quality standard (0.8 ppm).

According to the XRD analysis (see Figure 10), there was no difference between the samples of the same ratios of GBFS to MgO after fluoride sorption experiments and after hydration experiments. It is the same as hydration experiments that more brucite and hydrotalcite were precipitated after fluoride sorption for two weeks (Fig.10b) than for one week (see Figure. 10a).

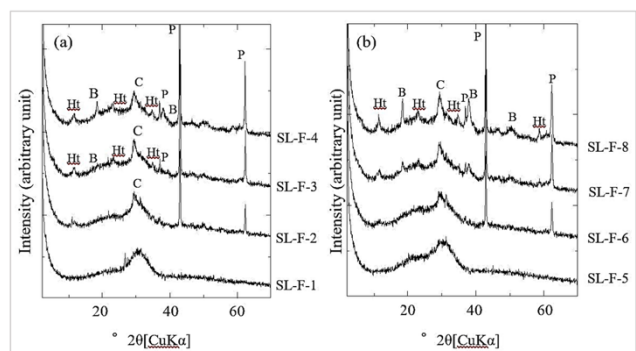


Figure 10: X-ray diffractograms of GBFS with different ratios of MgO after fluoride sorption for one (a) and two weeks (b) (Note: Ht-hydrotalcite; B-brucite; C-calcite; P-periclase).

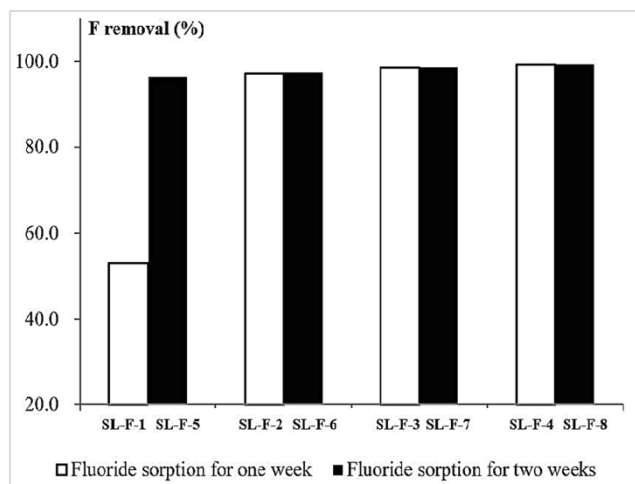


Figure 11: Fluoride removal efficiency of GBFS with addition of different ratios of MgO after fluoride sorption for one and two weeks.

In the case of GBFS without MgO addition, its fluoride removal efficiency (see Figure 11) was about 53% after fluoride sorption for one week (see Figure 10a). The fluoride removal efficiency (over 97%) could be greatly enhanced if MgO was added. As the MgO quantity reached 30%, the remaining fluoride met the Japanese water quality standard which is 0.8 ppm. The fluoride removal efficiency of GBFS without MgO addition reached about 96% after fluoride sorption for two weeks. In addition, fluoride removal efficiency also increased slightly as the amount of MgO addition increased.

According to the XRD analysis, there was no difference in mineralogy between the samples of the same ratios of T-CFA to Mg nitrate after fluoride sorption experiments and after hydration experiments. Since the T-CFA itself showed high fluoride sorption capacity (97.0%), the addition of Mg nitrate (10% to 25%) didn't affect fluoride removal efficiency, ranging from 96.7 to 97.1% after sorption for one week. The fluoride removal efficiency of the T-CFA samples with Mg nitrate addition after two weeks ranged from 97.0 to 97.7%.

Leachability of Fluoride after hydration

To gain better understanding of the leachable amount of fluoride by water, NH₄Cl and KCl solutions after fluoride sorption experiments, Equation 1 was used to calculate the leachable percentage of fluoride from fluoride-laden solid samples. In equation 1, L is the leached percentage of fluoride, C₀ is 100 ppm, C₁, V₁ and W₁ are the equilibrium concentration (ppm), liquid volume (ml) and solid weight (g) of the fluoride sorption experiments. C₂, V₂ and W₂ are the leached fluoride concentration, liquid volume and solid weight of the leaching tests. The leached fluoride using DI water was ascribed to water-soluble fluoride. While the difference in leached fluoride between the water-based leaching and KCl solution-based leaching under the same conditions was ascribed to exchangeable fluoride.

$$L = \frac{C_2 \cdot V_2 \cdot W_1}{(C_0 - C_1) \cdot V_1 \cdot W_2} \times 100 \quad (\text{Equation 1})$$

The concentrations of the leached fluoride from T-CFA without or with MgO addition are shown in Table 5. Apparently, the addition of MgO into T-CFA was able to reduce the amount of leachable fluoride. For leaching tests using a ratio of 40ml/1g, the fluoride concentrations leached out from different T-CFA samples by DI water ranged from 0.38 to 0.63ppm, lower than the Japanese water

quality standard. However, when 0.1M KCl was used as the extractant, the fluoride concentrations leached out were in a range of 1.10 to 1.25ppm, exceeding the Japanese water quality standard. According to Equation 1, 3.8% to 6.4 % of the total sorbed fluoride was ascribed to water soluble fluoride, and 5.8% to 8.4% of the total sorbed fluoride was attributed to exchangeable fluoride. In the leaching tests using a ratio of 40ml/0.5g, the fluoride concentrations leached out from different samples by DI water ranged from 0.34 to 0.45ppm, lower than the Japanese water quality standard. The use of 0.01M KCl as the extractant showed the same leaching ability as DI water, and the leached fluoride concentrations were in the range of 0.33 to 0.46ppm, also lower than the Japanese water quality standard.

However, according to Equation 1, the leached fluoride ascribed to water soluble fluoride ranged from 6.9% to 9.1% of the total sorbed fluoride, higher than that of samples with lower liquid to solid ratio (40ml/1g). The exchangeable amount of fluoride was negligible when 0.01M KCl was the extractant. For the leaching test using 0.1M NH₄Cl, the liquid/solid ratio was 20ml/1g lower than the above-mentioned leaching tests, and the leached concentrations of fluoride were in the range of 0.21 to 0.57 ppm, accounting for 1.05 to 2.9% of the total sorbed fluoride. Table 5 also shows the results of leached fluoride from the samples of T-CFA with Mg nitrate addition. Compared to T-CFA without any Mg addition (FA-F-1), more fluoride was leached if Mg nitrated was added into T-CFA. Under the liquid/solid ratio of 40ml/1g, the leached fluoride concentration by DI water was in the range of 0.86 to 1.46 ppm, by 0.1 M KCl it was in the range of 1.84 to 2.38 ppm. Based on equation 1, the leached fluoride ascribed to water soluble fluoride ranged from 8.9 to 15.1% of the total sorbed fluoride, and 7.3 to 14.8% of the total sorbed fluoride was exchangeable. Under the liquid/solid ratio of 40ml/0.5g, the leached fluoride concentration by DI water was in the range of 0.58 to 0.96 ppm, by 0.01 M KCl it was in the range of 0.68 to 1.01 ppm. Based on equation 1, 8.9 to 15.1% of the total sorbed fluoride was water soluble, and 7.3 to 14.8% of the total sorbed fluoride was exchangeable.

According to the fluoride leaching results as shown in Table 5, the addition of MgO into GBFS significantly reduced the amount of leachable fluoride from GBFS. The leached fluoride concentration from SL-F-1 was 5.38 ppm, making up 50.7% of its total sorbed fluoride. From SL-F-2, SL-F-3 and SL-F-4, of which 10%, 20% and 30% of MgO were added, the leached fluoride concentrations were 1.96, 0.85, 0.40 ppm respectively, accounting for 10.1%, 4.3% and 2.0% of their sorbed fluoride respectively. The leached fluoride concentration from SL-F-5 was 5.91 ppm, making up 30.7% of its total sorbed fluoride. From SL-F-6, SL-F-7 and SL-F-8, of which 10%, 20% and 30% of MgO were added, the leached fluoride concentrations were 1.01, 0.38, 0.18 ppm respectively, accounting for 5.2%, 2.0% and 0.9% of their sorbed fluoride respectively.

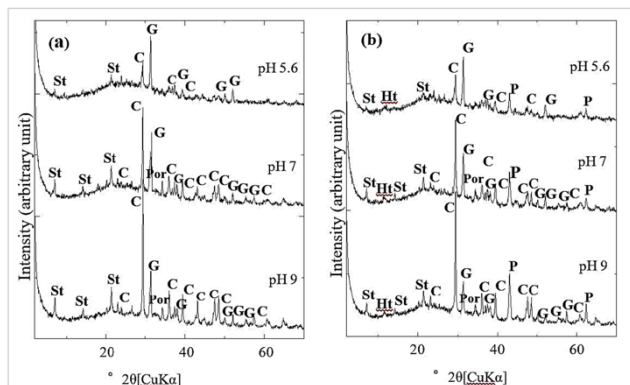


Figure 12: Selective dissolution of T-CFA samples with or without MgO addition after fluoride sorption for two weeks using different pHs: (a) FA-F-5; (b) FA-F-6; (c) FA-F-7; (d) FA-F-8 (Note: Note: St-stilpnomelane; Hc-hydrocalumite; C-calcite; G-gehlenite; Por-portlandite; Ht-hydrotalcite; B-brucite; P-periclase)

The selective dissolution of the samples of T-CFA with or without MgO addition after fluoride sorption for two weeks was performed. The mineralogical changes reflected by XRD analysis are shown in Figure 12, and leached fluoride concentrations are summarized in Table 5.

Table 5: Fluoride leaching and selective dissolution

Sample name	DI Water (40mL/1.0g; 25°C; 180 rpm; 5h)	0.1M KCl (40mL/1.0g; 25°C; 180 rpm; 5h)	DI Water (40mL/0.5g; 25°C; 180 rpm; 24h)	0.01M KCl (40mL/0.5g; 25°C; 180 rpm; 24h)	0.1 NH ₄ Cl (20mL/1g; 160 rpm; 18h)	pH for selective dissolution		
						pH 9	pH 7	pH 5.6
SL-F-1→SL-F-4	-	-	-	-	5.38→0.4 0	-	-	-
SL-F-5→SL-F-8	-	-	-	-	5.91→0.1 8	-	-	-
FA-F-1→FA-F-4	0.58→0.4 2	1.25→1.1 6	0.42→0.45	0.39→0.33	0.45→0.2 1			
FA-F-5→FA-F-8	0.63→0.4 1	1.19→1.1 0	0.37→0.35	0.35→0.39	0.23→0.3 0	1.28→1.2 9	1.17→1.4 7	1.15→1.18
FA-F-9→FA-F-12	0.86→0.8 9	2.29→2.0 2	0.70→0.83	0.86→0.87	-	-	-	-
FA-F-13→A-F-16	0.94→1.1 3	1.84→1.8 4	0.58→0.76	0.71→0.72	-	-	-	-

Note: The arrow symbol → signifies a step-wise progression tracking individual additive ratios matching the definitions in Tables 1 and 2. Leaching test operational conditions

According to the XRD analysis, most of the minerals became unstable when pH was less than 9. In FA-F-5, the hydrocalumite peak disappeared, and the peak intensity of some Ca-containing minerals such as stilpnomelane, portlandite, gehlenite decreased while the peak intensity of calcite became relatively stronger at pH 9; when pH reached 7, the peak intensity of calcite also started to decrease; at pH 5.6, the preserved minerals were calcite, gehlenite and small amount of stilpnomelane, in addition, the peak intensity of gehlenite became stronger than that of calcite. In FA-F-6, although there was only small amount of hydrotalcite, it was not dissolved while the dissolution of periclase was observed as the pH decreased from 9 to 5.6; the changes of the other minerals in FA-F-6 were like in FA-F-5. In FA-F-7, there were brucite and more hydrotalcite compared to FA-F-6; hydrotalcite was unchanged when pH decreased from 9 to 5.6; but the peak of brucite disappeared at pH 5.6; the peak of stilpnomelane disappeared at pH 7; portlandite was preserved at pH 5.6; the changes of the other minerals in FA-F-7 were the same as in FA-F-6. Although dissolution occurred in most of the minerals in FA-F-8, the peaks of all the minerals except stilpnomelane which disappeared at pH 9 was preserved to some extent as pH decreased from 9 to 5.6.

During the process of dissolution of some minerals, some of the sorbed fluoride was released. In FA-F-5, the leached fluoride concentrations were 1.28, 1.17 and 1.15 ppm, accounting for 26.3%, 24.1% and 23.6% of the total sorbed fluoride, at pH 9, 7 and 5.6 respectively. In FA-F-6, the leached fluoride concentrations were 1.39, 1.26 and 1.18 ppm, accounting for

28.3%, 25.5% and 23.9% of the total sorbed fluoride, at pH 9, 7 and 5.6 respectively. In FA-F-7, the leached fluoride concentrations were 1.29, 1.70 and 1.26 ppm, accounting for 26.1%, 34.4% and 25.4% of the total sorbed fluoride, at pH 9, 7 and 5.6 respectively. In FA-F-8, the leached fluoride concentrations were 1.29, 1.47, and 1.18 ppm, accounting for 25.9%, 29.5% and 23.7% of the total sorbed fluoride, at pH 9, 7 and 5.6 respectively.

CONCLUSION

This study evaluated GBFS and coal fly ash as supplementary cementitious binders for radioactive waste stabilization and it specifically focused on controlling hydrotalcite formation through Mg addition to immobilize arsenate and fluoride. The findings of the study indicated that the slightly soluble MgO is superior to Mg nitrate for maintaining high pH (>12) and stabilizing hydrotalcite and brucite. MgO addition (10%–30%) significantly improves anion removal in GBFS. Hydrotalcite phases remain stable down to pH 5.6, offering safer long-term sequestration than Ca-minerals. The demonstrated immobilization of anionic species based on the leachability results suggest high potential for the stabilization of radioactive anionic wastes. Hence, the findings of this study contribute valuable insights into the valorization of iron slag and coal fly ash for the solidification and stabilization of radioactive waste by controlling their long-term geochemical evolution. Optimizing these specific geochemical pathways may improve the

utilization of iron slag and coal fly ash that will contribute to the development of highly effective engineered barriers for sustainable management of nuclear waste.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interest.

CONTRIBUTIONS OF INDIVIDUAL AUTHORS

EO: Conceptualization, Writing, Methodology, Validation, Formal Analysis, Supervision, Funding acquisition, Data Curation, Resources. SB.: Analyzing, Writing-review & Editing. MA: Formal Analysis, Review. LX: Investigation, Formal Analysis, Writing, Review. TS: Investigation, Formal Analysis, Visualization.

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