



## Coal fly ash as a potential fixation reagent for radioactive wastes



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### HIGHLIGHTS

- Fly-ash acts as a blocking barrier for radionuclide cations diffusion.
- Fixation of the radionuclides is via  $-AlO_2^-/-SiO_3^-$  anions at the fly ash surface.
- A novel  $Sr^{90}$  fixation mode via precipitation and adsorption to the fly ash is found.

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### ABSTRACT

Israel produces  $\sim 1.3$  Mt/year of fly ash (FA), a byproduct of its coal-fired power plants. Due to increasing environmental regulations, these imported coals are processed to reduce the sulfur concentration ( $\sim 0.6\%$ ). These processing methods result in a material that has an enriched alkali/alkali earth component with pozzolanic and basic properties ( $pH > 10.5$ ).

FAs are utilized worldwide, mainly as a cement additive for the construction industry. Recently, it was demonstrated that Class F FA can act as an excellent fixation reagent for acidic wastes from the phosphate or the oil regeneration industries. In the current work the potential utilization of Class F FAs as fixation reagents for low-activity radioactive waste from the nuclear industry was examined. Aqueous solutions containing radionuclide simulants: cesium ( $Cs^+$ ), strontium, ( $Sr^{2+}$ ), and cerium ( $Ce^{3+}$ ,  $Ce^{4+}$ ) were used as case studies with promising results. It is suggested that the primary fixation mechanism involves the aluminate/silicate anions at the FA surface. A novel experimental fixation approach utilizing the formation of carbonates is demonstrated and a new interaction mechanism is suggested based on the electrostatic interactions of the positively charged fine precipitates with the negatively charged FA surface.

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## 1. Introduction

Israel utilizes imported bituminous coal as a primary fossil fuel for power production ( $>63\%$  in 2013 [1]). Annually, the utilities consume  $\sim 13$  Mt of coal producing 183,000 tons of bottom ash (BA) and 1.3 Mt of FA [2]. The coals are imported mainly from South Africa but also from Colombia, Australia, Indonesia, and Russia [2] and contain  $\sim 10\%$  of inorganic mineral materials.

In line with Israel's strict environmental regulations regarding the emission of pollutants to air via the combustion process [3], the imported coal undergoes beneficiation (via washing with

water) to reduce the organic constituents; primarily sulfur (S) and phosphorous (P) [4] and some trace elements (e.g. Hg, Pb, and As). The result is that the FA produced is rich in alkali and alkali earth elements, pozzolanic with cementitious properties, and is considered to be a Class F FA [2] (which has a basic solution in contact with water). Consequently, when in contact with water, the FA is highly basic,  $pH > 10.5$  at Solid/Liquid ratio of 1/10, due to high lime content (CaO) in the FA. Currently, 100% of the ash (bottom and fly) produced [2] in Israel is utilized in the construction industry either as a cement additive (up to 10% weight content), road structural filler, or other minor applications (e.g. agriculture) [2,5–15]. Thus, it is economic value is rather low  $\leq 15$  \$/ton.

The possibility of using FA as an effective neutralization and fixation reagent for acidic wastes has been explored and suggested as a more significant economic value added as a utilization method [16–19].

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Several mechanisms for the fixation of metal ions and the FA surface have been previously suggested [20–23].

### 1.1. Cation-exchange

The surface of the FA particles contains several anionic functional groups mainly aluminates  $-O-AlO^-$  and silicates  $-O-SiO_2^-$ : which can behave as a cation-exchange material. Typical metal cations that can undergo fixation to the FA surface are mono- or divalent metal cations (e.g.,  $Cs^+$ ,  $Cd^{2+}$ ,  $Cu^{2+}$ , and  $Sr^{2+}$ ).

### 1.2. Coordinative bonding

Coordinative bonding is formed between the cation and non-bonding electrons of functional groups located at the surface of the FA particles. The cation behaves as a Lewis acid and the FA surface behaves as a Lewis base. This is a mechanism in which the Lewis base donating the lone pair of electrons forms a bond with the metal cation. This interaction is equivalent to the formation of a complex where the surface groups are the ligands. Energetically, it is a relatively strong bond, which can reach a strength of  $>150$  kJ/mol [24]. Typical metal cations that can undergo this interaction are  $Ce^{III}$ ,  $Ce^{IV}$ , or  $UO_2^{2+}$ .

The feasibility of this application has also been effectively demonstrated with industrial wastes. The acidic organic waste produced during regeneration processes of used motor oil (via Oleum extraction) yields extremely acidic waste,  $>10$  M  $H^+$  with a high concentration of heavy and toxic metals [17] along with the acidic waste (0.1–1 M) from the phosphate industry (a byproduct of the phosphate rock dissolution process via either sulfuric or hydrochloric acids [16] were both effectively neutralized with a FA fixation method. In both types of wastes (motor oil and phosphate), fixation with FA produces a grey sand-like aggregate. The effectiveness of the toxic and heavy metal content fixation was determined using European Directive [25], the USEPA TCLP 1311 [26], and CALWET [27] leaching procedures. Furthermore, the leaching of trace elements from the scrubbed product is within the Israeli drinking limits criteria [28].

These initial findings demonstrated fixation of acidic and heavy metals in Class F FAs and therefore have the potential ability to reduce the costs of low activity radioactive wastes treatment produced in the nuclear energy industry.

Unlike other industrial wastes, the hazard level of all nuclear waste – its radioactivity – diminishes with time. Each radionuclide contained in the waste has a half-life – the time taken for half of its atoms to decay, and, thus for it to lose half of its radioactivity (assuming that the product of decay are not radioactive by themselves). The half-life of radionuclides can vary from seconds to millions of years (see below). Radionuclides with long half-lives tend to be alpha and beta emitters – making their handling easier – while those with short half-lives tend to emit the more penetrating gamma rays. Eventually all radioactive wastes decay into non-radioactive elements. The more radioactive an isotope is, the faster it decays.

The main objective in managing and disposing of radioactive (or other) waste is to protect people and the environment. This means isolating or diluting the waste so that the rate or concentration of any radionuclides returned to the biosphere is harmless. To achieve this, practically all wastes are contained and managed – some clearly need deep and permanent burial. From nuclear power generation, none is allowed to cause harmful pollution. High-level wastes, which contain 19% of the total activity of accumulated liquid radioactive wastes, are the most dangerous. The activity of high-level wastes is determined by the high concentrations of isotopes  $^{137}Cs$ ,  $^{134}Cs$ , and  $^{90}Sr$ , as well as by the presence of long-lived actinides. The ecological risk due to intermediate-level wastes is

associated with the fact that the activity of these wastes comprises the main fraction of the total activity of all accumulated liquid radioactive wastes. [29].

FA has demonstrated fixation properties and has the potential to reduce storage and treatment costs of various wastes. It can also potentially service the nuclear industry by partially substituting other storage materials (concrete, bitumen), which are currently utilized. The current work focuses on the ability of the FA to fixate the following types of radionuclides occurring in typical radioactive wastes [30–34]:

- (i) **Cs<sup>137</sup>** is one of the main nuclear fission byproducts of **U<sup>235</sup>** in nuclear power plants (with a half-life of 30.17 years [31]). This radionuclide decays via emission of  $\beta$  rays (0.19 MeV) to form metastable nucleus of Barium (137 m) – **Ba<sup>137m</sup>**, which further decays relatively fast (2.6 min) via emission of  $\gamma$  rays (0.60 MeV) to the stable isotope of Barium **Ba<sup>137</sup>**.
- (ii) **Sr<sup>90</sup>** This radionuclide is also one of the major nuclear fission byproducts of **U<sup>235</sup>**. Its half-life is 28.90 years [30] and it decays via  $\beta$  irradiation emission (0.546 MeV) to a stable isotope of Yttrium **Y<sup>90</sup>**.

These two radionuclides have a medium half-life and have to be stored for centuries until decaying to a low-level background radiation.

- (iii) **Actinides** The Actinides, which are one of the main byproducts during fission, are all radioactive. They are usually formed via neutron capture by U isotopes (mainly **U<sup>238</sup>**) and have relatively very long half-lives. These actinides are f-block elements, filling the 5f electron shell and are also  $\alpha$  emitters. Typical actinides are the plutonium – **Pu** or Americium – **Am** [35].

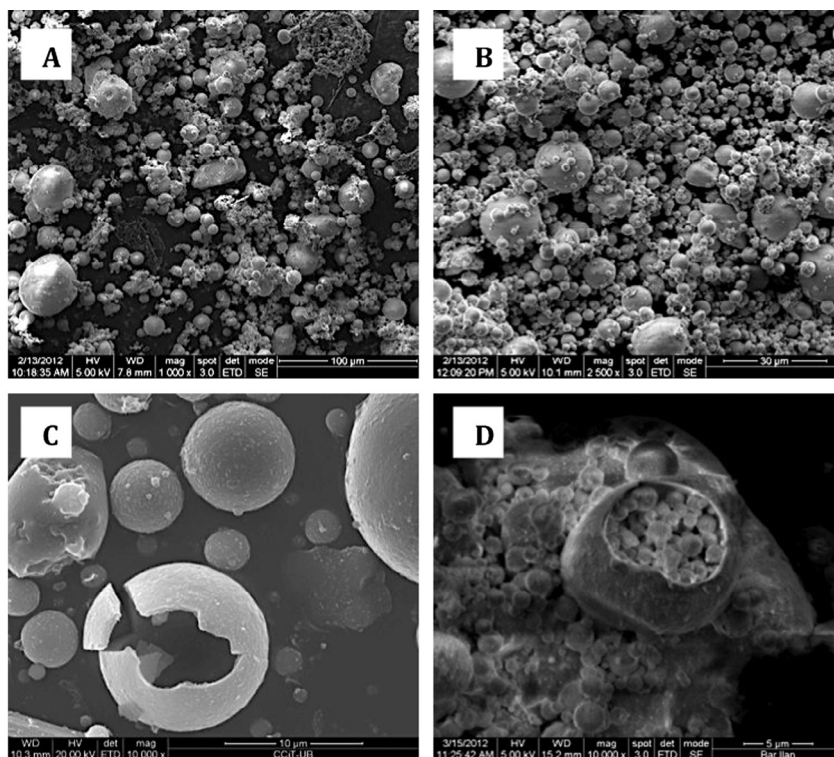
## 2. Experimental

### 2.1. Fly ash characterization

The FA used in the current study is the combustion waste product from South African (SA) and Colombian (CO) coals used in Israel and were supplied by the Israeli Electricity Company. In this paper, the two FA types will hereby be referred to (adding a SA or CO prefix) as SAFA or COFA. The SA and CO coals after beneficiation contain 13.9 wt.% and 8.7 wt.% ash and have a spatial density of  $0.98$  g/cm<sup>3</sup> and  $0.85$  g/cm<sup>3</sup>, respectively. The ambient air quality standards used in Israel require a low content of S and P in the combustion process. The FA product of these pretreated coals leads to the enrichment of the ash with alkali and alkali earth elements, mainly Ca. The FA particles [11,36] are spherical and have a diameter of between 3 and 250  $\mu$ m (Fig. 1). Moreover, XRD analysis was performed on both the SAFA and the COFA (Fig. S1).

The FA mainly contains two different types of spherical particles. Cenospheres (Fig. 1C) are hollow “glass bubbles” [37] of aluminosilicates. These particles also contain carbon dioxide or nitrogen which give the ash lightweight properties [37–39]. The second type are the Pleurospheres [40] (Fig. 1D) which are “hollow glass bubbles” filled with smaller glassy particles. In addition, some minerals such as spinels are also present within the FA [41]. FA particles have a relatively large surface area for a non-porous material [2] ( $1.05 \pm 0.1$  m<sup>2</sup>/g for SAFA and COFA). The averaged chemical analysis of both the SAFA and COFA is presented in Table 1.

EDAX analysis of the FA surface functionality presented in Fig. 1 show that SAFA and COFA have similar concentrations (surface coverage) of Si and Al.



Wt.%	O	Al	Si	Na	Mg	P	K	Ca	Ti	Fe	Total
<b>SAFA (image A)</b>	49.0	17.8	24.4	0.4	1.1	0.7	0.4	4.0	0.7	1.5	100
<b>COFA (image B)</b>	41.0	17.1	27.0	4.7	1.2	N.A.	2.2	2.1	0.9	3.8	100

\*\* error factor  $\pm 0.1\%$

**Fig. 1.** SEM images of: (a) South African fly ash, (b) Colombian fly ash, (c) South African fly ash cenospheres and (d) Colombian fly ash Pleurospheres.

**Table 1**

Chemical composition of major (wt.%) and trace elements (mg/kg) of South African fly ash and Colombian fly ash.<sup>a</sup>

Major elements	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	LOI <sup>b</sup>	Total	
SAFA	41	31	1.6	3.1	9.5	2.2	0.8	0.2	2.4	0.7	5.0	97.5	
COFA	56	23	1.0	7.1	3.4	1.7	1.6	3.1	0.3	0.9	2.3	100.4	
Trace elements	Ag	As	Ba	Be	Cd	Co	Cr	Cu	Mn	Ni	Sr	Hg	Pb
SAFA	14	<10	2,160	9.43	<2	40	150	77	440	68	3,250	0.4	80
COFA	9.5	<10	3,210	5.07	2	27	133	60	330	70	1,050	0.2	78

<sup>a</sup> Both Fly ashes were homogenized, several analyses were carried out for each fly ash.

<sup>b</sup> LOI = loss on ignition.

In line with the average chemical composition (Table 1), the XRD bulk analysis of the FA presented in Fig. S1 shows that the primary minerals present in both types of ash are Mullite ( $3\text{Al}_2\text{O}_3-2\text{SiO}_2$ ) and Quartz ( $\text{SiO}_2$ ).

Moreover, the bulk Quartz/Mullite ratio is different for either FA. In the SAFA, Mullite is the dominant mineral while COFA has more Quartz. Surprisingly, despite this difference in the bulk composition, the EDAX results (Fig. 1) seem to indicate (within the experimental error) that surface content of these two elements (in the COFA and SAFA) is similar. The high concentration of Al and Si at the surface is present in the form of aluminates and silicate groups.

Finally, these surface groups (aluminates and silicates) have a significant negative surface charge, which is confirmed by

measuring the zeta potential. The results from the zeta potential analysis at basic pHs are presented in Fig. 2.

## 2.2. Chemicals

Due to the high cost of operation when working with radionuclides, accepted simulants utilized in nuclear research were selected for these studies. The following four simulants, Cs<sup>133</sup> as simulant to the radionuclide Cs<sup>137</sup>, Sr<sup>88</sup> as simulant to the radionuclide Sr<sup>90</sup>, and Ce<sup>3+</sup> and Ce<sup>4+</sup> as simulants to the Actinide group were selected after consulting with researchers from the Nuclear Research Center Negev (NRCN). The simulants salts chosen were CsNO<sub>3</sub>, Sr(NO<sub>3</sub>)<sub>2</sub>, Ce(NO<sub>3</sub>)<sub>3</sub>, and Ce(SO<sub>4</sub>)<sub>2</sub>·2(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>·2H<sub>2</sub>O. All salts used were analytical grade and purchased from Sigma/

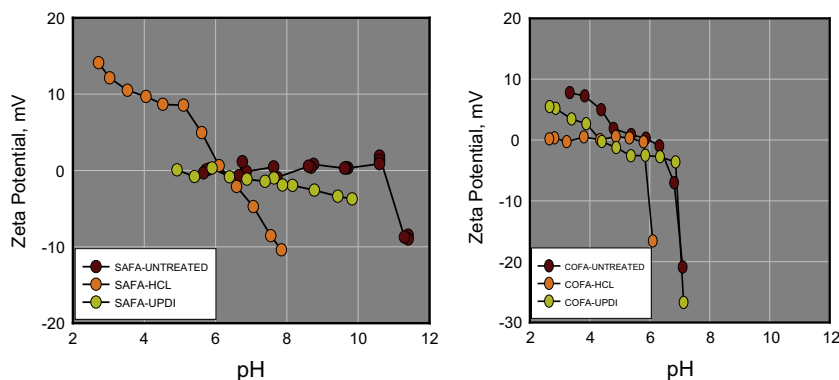


Fig. 2. Zeta potential measurements of untreated/treated South African fly ash/Colombian fly ash.

Aldrich or Merck. Water used in the study was DDW (Double Distilled Water) using a Tri-ion system with a measured resistance larger than 10 Mohms/cm.

### 2.3. Analytical methods

Solution concentrations of  $\text{Sr}^{2+}$ ,  $\text{Cs}^+$ ,  $\text{Ce}^{3+}$ , and  $\text{Ce}^{4+}$  were determined with Inductively-Coupled Plasma Atomic Emission Spectrometry (ICP-AES) model Thermo Jarrell Ash IRIS as well as Inductively-Coupled Plasma Mass Spectrometry (ICP-MS) model Thermo Electron Corporation X-Series. Ion chromatograph (Dionex model DX-500) was used to determine  $\text{Cs}^+$  concentrations. Six Calibration solutions were prepared from a M-solution (Manufactured by Fischer) of 1000 ppm: 0.05 ppm, 0.1 ppm, 0.5 ppm, 1 ppm, 10 ppm, and 20 ppm. The detection limit was <0.05 ppm for all simulants. A typical sample for ICP analysis was prepared by passing it through 0.45- $\mu\text{m}$  Whatman puradisc FP 30 CA-S filters. After the mixing period, the fly ash was filtered from the slurry and a sample from the solution was taken and acidified with 0.1% vol. of concentrated  $\text{HNO}_3$  to prevent precipitation. Finally the concentration of the desired element was analyzed with ICP-AES.

Orbital Shakers from Cocono, model TS-400 were used for the fixation procedure.

Samples composition and morphology was analyzed by a MK2 Quanta 200 Scanning Electron Microscope with energy dispersive X-ray analyzer (SEM-EDAX).

XRD patterns were collected using a Bruker D8 Advance diffractometer with monochromatic  $\text{Cu K}\alpha_{1,2}$  radiation ( $\lambda = 1.5405$ ) operated at 40 kV and 40 mA. The primary parallel X-ray beam was generated by a Göbbel mirror and the scattered beam was analyzed by a Sol-X detector with the following scanning parameters: from  $4^\circ$  at  $60^\circ$  of  $2\theta$ , a step size of  $0.05^\circ$ , and time per step of 3 s.

Zeta potential measurements were carried out on a Malvern Zeta Sizer Nano ZS. This device employs a combination of laser Doppler velocimetry and phase analysis light scattering (PALS) for measuring the zeta potentials. An automatic titrator was used to adjust the pH.

### 2.4. Standard fixation experimental procedure

A standard fixation protocol [42] was used for the fixation experiments. The experimental protocol contains the following four stages:

- I. A simulant solution standard was prepared of the trace element (Ce, Sr, or Cs). The volume was calculated to be sufficient for 25 experiments to reduce standard preparation

error. The concentration of each standard was validated by ICP-AES.

- II. The solution was mixed with SAFA or COFA in a 500-ml PET bottle, using a fixed S/L (solid to liquid) ratio.
- III. The slurry was then shaken in the orbital shakers at 250 rpm for different periods of time.
- IV. Sample collection – the mixed slurry was settled for 15 min, and then a 10 ml sample from the middle of solution was collected. After that, the sample was filtered with 0.45- $\mu\text{m}$  filter and acidified with 0.1% vol. of concentrated  $\text{HNO}_3$ .

## 3. Results

### 3.1. Fixation of $\text{Ce}^{3+}$ and $\text{Ce}^{4+}$ with SAFA and COFA/standard fixation method

Solutions containing 1, 19, or 20 ppm of  $\text{Ce}^{3+/4+}$  ions were prepared from  $\text{Ce}(\text{NO}_3)_3$  or  $\text{Ce}(\text{SO}_4)_2 \cdot 2(\text{NH}_4)_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$  salts. The solutions were acidified with HCl to pH 2 in order to avoid reduction of the ions or formation of cerium precipitates [43].

The fixation of the Ce ions was studied as a function of shaking time as shown in Table 2 (samples 1–11 ( $\text{Ce}^{3+}$ ), samples 12–22 ( $\text{Ce}^{4+}$ )).

The  $\text{Ce}^{3+/4+}$  ions were trapped by the FA particles and the concentration of cerium in the  $[\text{Ce}]_f$  in the scrubbed solution is below the detection limit. Moreover, the fixation procedure is fast, reaching completion in the course of the first hour.

### 3.2. Fixation of $\text{Cs}^+$ with SAFA and COFA/standard fixation methods

Solutions of 10 or 20 ppm of  $\text{Cs}^+$  ions were prepared from  $\text{CsNO}_3$  salt. Analysis of  $[\text{Cs}^+]_f$  in the filtrate was carried with the ICP-AES spectrometers or with the Dionex ion-chromatograph (Table 3).

In all experiments it was found that  $\sim 30\%$  ( $0.31 \pm 0.11$ )  $\text{Cs}^+$  ions have been trapped by the FA particles.  $[\text{Cs}]_f$  was reduced on average by  $5.1 \pm 0.57$  ppm regardless of initial concentration.

### 3.3. Fixation of $\text{Sr}^{2+}$ with SAFA and COFA/standard fixation methods

Solutions of 20 ppm of  $\text{Sr}^{2+}$  were prepared from  $\text{Sr}(\text{NO}_3)_2$  salt. The first set of experiments was performed using the same procedure as carried out with the  $\text{Cs}^+$  and  $\text{Ce}^{3+/4+}$  fixation experiments. The filtrate was analyzed for strontium with the ICP-AES spectrometer (Table 4).

The results in Table 4 clearly indicate that there was no of fixation of the Sr cations. Furthermore, an appreciable amount of Sr ions leaches out from the FA into the solution (due to the high concentration of the strontium in the SAFA  $\sim 0.3$  wt.%, Table 1). Moreover, in a more acidic environment (either 0.1 M or 1 M

**Table 2**Fixation of Ce<sup>3/4+</sup> with South African fly ash/Colombian fly ash in a 1:20 ratio S/L<sup>a</sup> (10 g FA:200 ml solution).

#	FA type	Ion	FA weight (g)	Shaking period (h)	[Ce] <sub>0</sub> (ppm) <sup>a</sup>	[Ce] <sub>f</sub> (ppm) <sup>a</sup>	% Fixation	ΔpH (pH <sub>final(afterFAcontact)</sub> – pH <sub>initial</sub> )
1	SAFA	Ce <sup>3+</sup>	10	10 min	19	16.3	14.2%	1.4
2	SAFA	Ce <sup>3+</sup>	10	30 min	19	9.5	50%	1.2
3	SAFA	Ce <sup>3+</sup>	10	1	19	<0.05	~100%	3.6
3	SAFA	Ce <sup>3+</sup>	10	5	19	<0.05	~100%	0.3
4	SAFA	Ce <sup>3+</sup>	10	8	19	0.9	>95%	0.4
5	SAFA	Ce <sup>3+</sup>	10	24	19	<0.05	~100%	0.2
6	COFA	Ce <sup>3+</sup>	10	5	19	<0.05	~100%	0.6
7	COFA	Ce <sup>3+</sup>	10	8	19	<0.05	~100%	0.5
8	COFA	Ce <sup>3+</sup>	10	24	19	<0.05	~100%	0.7
9	SAFA	Ce <sup>3+</sup>	10	5	1	<0.05	~100%	0.3
10	SAFA	Ce <sup>3+</sup>	10	8	1	<0.05	~100%	0.4
11	SAFA	Ce <sup>3+</sup>	10	48	19	<0.05	~100%	0.3
	CAL	Ce <sup>3+</sup>	0	0	19	19	0	1.7
12	SAFA	Ce <sup>4+</sup>	10	10 min	20	5.1	~75%	1.2
13	SAFA	Ce <sup>4+</sup>	10	30 min	20	3.7	~82%	1.8
14	COFA	Ce <sup>4+</sup>	10	10 min	20	6.5	~68%	0.9
15	COFA	Ce <sup>4+</sup>	10	30 min	20	7.6	~62%	0.4
16	SAFA	Ce <sup>4+</sup>	20	5	1	<0.05	~100%	0.2
17	SAFA	Ce <sup>4+</sup>	20	24	20	<0.05	~100%	0.5
18	SAFA	Ce <sup>4+</sup>	20	96	20	<0.05	~100%	0.4
19	SAFA	Ce <sup>4+</sup>	20	30	1	<0.05	~100%	0.6
20	COFA	Ce <sup>4+</sup>	20	48	20	<0.05	>90%	0.5
21	COFA	Ce <sup>4+</sup>	20	72	20	<0.05	~100%	0.4
22	COFA	Ce <sup>4+</sup>	20	96	20	<0.05	~100%	0.3
	Cal	Ce <sup>4+</sup>	0	0	20	20	0	1.3

\*\* Detection limit &lt; 0.05 ppm.

<sup>a</sup> [Ce]<sub>0</sub> concentration before mixing with FA, [Ce]<sub>f</sub> concentration (after fixation procedure) in the filtrate.**Table 3**Fixation of Cs<sup>+</sup> with South African fly ash/Colombian fly ash in a 1:20 ratio (S/L).

#	FA type	FA weight (g)	Shaking period (h)	[Cs] <sub>0</sub> (ppm) <sup>a</sup>	[Cs] <sub>f</sub> (ppm) <sup>a</sup>	Δ[Cs]	% Fixation	ΔpH (pH <sub>final(afterFAcontact)</sub> – pH <sub>initial</sub> )
1	COFA	20	1	20	15.1	–4.9	~25%	3.7
2	COFA	20	5	20	15.6	–4.4	22%	3.9
3	COFA	20	24	20	14.1	–5.9	~30%	3.6
4	COFA	20	24	10	5.3	–4.7	~24%	4.1
5	COFA	20	24	10	4.4	–5.6	28%	3.7
6	SAFA	20	1	20	14.9	–5.1	~26%	5.6
7	SAFA	20	5	20	14.4	–5.6	28%	5.8
8	SAFA	20	5	20	15.7	–4.3	~22%	5.4
9	SAFA	20	24	20	14.5	–5.5	~28%	5.5
10	SAFA	20	24	10	7.2	–2.8	28%	5.5
11	0	0	0	20	20	0	0	6.0

<sup>a</sup> [Cs]<sub>0</sub> concentration before mixing with FA, [Cs]<sub>f</sub> concentration (after fixation procedure) in the filtrate.**Table 4**Fixation of Sr<sup>2+</sup> with South African fly ash in a 1:20 ratio (S/L).

#	SAFA weight (g)	Mixing period (h)	[Sr] <sub>0</sub> (ppm)	[Sr] <sub>f</sub> (ppm)	% Fixation
1	20	5	9.9	16.8	–169%
2	20	96	9.9	34.4	–347%
3	20 + 1 M HCl	30	9.9	551.3	~–5570%
4	20 + 0.1 M HCl	24	9.9	16.8	–170%
5	0	0	10	9.9	N.A.

\* [Sr]<sub>0</sub> concentration before mixing with FA, [Sr]<sub>f</sub> concentration (after “fixation” procedure) in the filtrate.

HCl) an increased leaching of strontium occurs as a result of dissolution. As the COFA also contains appreciable concentrations of strontium (~0.1 wt.%, Table 1), no experiments using this procedure were carried out with the COFA.

### 3.4. Fixation of Sr<sup>2+</sup> with SAFA and COFA/adapted carbonate fixation method

In order to utilize FA for the fixation of strontium waste, a different approach is required. A possible method is to precipitate

the Sr<sup>2+</sup> ions as an insoluble salt and trap it on the surface or in the FA particle pore system. One cost-effective direction is the formation of a carbonate salt; SrCO<sub>3</sub> (K<sub>sp(SrCO3)</sub> = 5.60 × 10<sup>–10</sup> M<sup>2</sup> [44]). In order to precipitate fine SrCO<sub>3</sub> particles – strontianite, which might adhere to the surface of the FA particles, three possible methods were investigated:

- (i) Addition of 0.5 g solid sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) to the FA/Sr<sup>2+</sup> solution mixture prior to the fixation process.
- (ii) Bubbling of atmospheric air (which contains ~400 ppm carbon dioxide –CO<sub>2</sub>) through the FA/Sr<sup>2+</sup> solution mixture (as shown in Fig. S2). Since the solution is very basic (pH > 10.5 see above) the CO<sub>2</sub> will be trapped in the solution, and will form carbonate anions CO<sub>3</sub><sup>2–</sup>, which subsequently, will precipitate the Sr<sup>2+</sup> ions as the carbonate salt.
- (iii) Combined addition of 0.5 g Na<sub>2</sub>CO<sub>3</sub> and bubbling of atmospheric air (CO<sub>2</sub>) into the FA/Sr<sup>2+</sup> solution.

The precipitation procedure can be summed up by the following set of reactions:

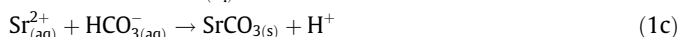


**Table 5**  
Fixation of Sr<sup>2+</sup> with FA in a 1:20 ratio (S/L) as either Na<sub>2</sub>CO<sub>3</sub> precipitates or air bubbling.

#	FA type	Carbonate source	FA weight (g)	Mixing period (h)	[Sr] <sub>0</sub> (ppm)	[Sr] <sub>f</sub> (ppm)	% Fixation	Final pH
1	SAFA	Na <sub>2</sub> CO <sub>3</sub> addition	20	5	9.9	0.15	~99%	12.5
2	SAFA	Na <sub>2</sub> CO <sub>3</sub> addition	20	5	9.9	0.15	~99%	12.6
3	SAFA	Air bubbling	20	24	9.9	0.16	~99%	12.6
4	SAFA	Air bubbling	20	24	9.9	0.12	~99%	12.4
5	SAFA	Air bubbling + Na <sub>2</sub> CO <sub>3</sub> addition	10	5	13.8	<0.5	~96%	12.7
6	COFA	Air bubbling + Na <sub>2</sub> CO <sub>3</sub> addition	10	5	13.8	1.0	~93%	10.7
7	N.A.	Air bubbling	0	24	10	9.9	N.A.	12.5
8	N.A.	Air bubbling	0	24	13.8	13.8	N.A.	12.4
9	N.A.	Na <sub>2</sub> CO <sub>3</sub> addition	0	5	10	9.9	N.A.	12.5

\*[Sr]<sub>0</sub> concentration before mixing with FA, [Sr]<sub>f</sub> concentration after mixing with FA.

\*\*Detection limit < 0.5 ppm.



In one set of experiments, 0.5 g of Na<sub>2</sub>CO<sub>3</sub> were added to the mixture of the FA/Sr<sup>2+</sup> solution (1:20 S/L ratio) and in a second set, air was bubbled through the same

Mixture of FA/Sr<sup>2+</sup> solution to dissolve CO<sub>2</sub> from the air into the basic solution and in the third set, a combination of both the carbonate salt addition and air bubbling was performed. The samples were collected and processed for ICP analysis and the results are presented in Table 5.

At pH ~ 12.5 the total concentration of Sr is expected to precipitate as SrCO<sub>3</sub>. Furthermore, the SrCO<sub>3</sub> particles formed only under basic conditions in the absence of FA (Table 5, samples 7–9) pass through the 0.45-μm Teflon filter and no apparent change in the solution [Sr] is detected.

The results in Table 5 indicate that in all the SAFA experiments no strontium ions are detected (within experimental error) in the analyzed extracted solutions. This indicates that all the Sr<sup>2+</sup> ions were precipitated as an insoluble carbonate salt that either has a particle size greater than 0.45 μm or that the particles formed adhered to the FA surface.

#### 4. Discussion

Fundamentally, the ability of FA to serve as an efficient low-cost fixation material is attributed to the high concentration of alumina and silica functional groups present at the surface of the FA particles. The most abundant anionic groups at the surface are the silicates (–O–SiO<sub>2</sub><sup>–</sup>) or the aluminates (–O–AlO<sup>–</sup>) groups as can be observed in the EDAX analysis (Si or Al) presented in Fig. 1. Furthermore, the relatively large surface area (>1 m<sup>2</sup>/g) of the FA particles was also determined to retain a significant negative charge in a basic solution (Fig. 2). These functional groups have different charges as a function of pH and can undergo interactions with ions through several reported mechanisms. In the current work it is apparent that there are 2 standard mechanisms involving the same functional groups at play for each of the different simulants. For the Cs<sup>+</sup> and the Ce<sup>3+/4+</sup> ions the standard fixation models such as cation exchange or coordinative bonding are valid.

There is a pronounced difference between the fixation capability of the same FA substrate towards Cs<sup>+</sup> (Table 4) compared with Ce<sup>3+/4+</sup> ions (Table 3). Foremost, the interaction in both cases is concentration dependent and almost instantaneous. Surprisingly, while the initial concentration of both simulants is ~20 ppm, it appears that the ability of the FA substrate to fixate cerium ions is greater. This can be assumed by the complete (within experimental error) fixation of the Ce<sup>3+/4+</sup> ions vs. only ~30% (0.31 ± 0.11) of the Cs<sup>+</sup>

ions. However, the assumption that the surface functionalities responsible for this fixation effect are the same and remain constant suggests that different mechanisms are at play. One possible explanation for this difference could be explained by simply taking the ionic radii of the ions into consideration. The ionic radius of Cs<sup>+</sup> is 181 pm (pico-meter, or 1.81 Å) as opposed to that of Ce<sup>3+/4+</sup> which are considerably smaller with a, respectively, 115 and 101 pm (or 1.15, 1.01 Å). The respective size of the cesium ions are on average ~68% larger than those of the cerium ions. This difference might perhaps explain the reduced capacitance of the FA. Although, the difference in bulk pH of the solution is a more likely candidate for these differences as a result of the changes in surface acidity (deprotonating –XH groups on the surface) affecting the available binding groups [45]. Obviously this is not an adequate explanation as one would expect that at a basic pH the fixation would increase (i.e. Cs<sup>+</sup>) while at the acidic pH (i.e. Ce<sup>3+/4+</sup>) the fixation would decrease as a result of a more significant change in the surface functionalities along the lines of the pH effect on the measured zeta potentials (Fig. 2).

It is likely that the fixation mechanism for each of the ions is different. Cs<sup>+</sup> is expected to interact with the FA surface in a cation exchange mechanism (Fig. 3A).

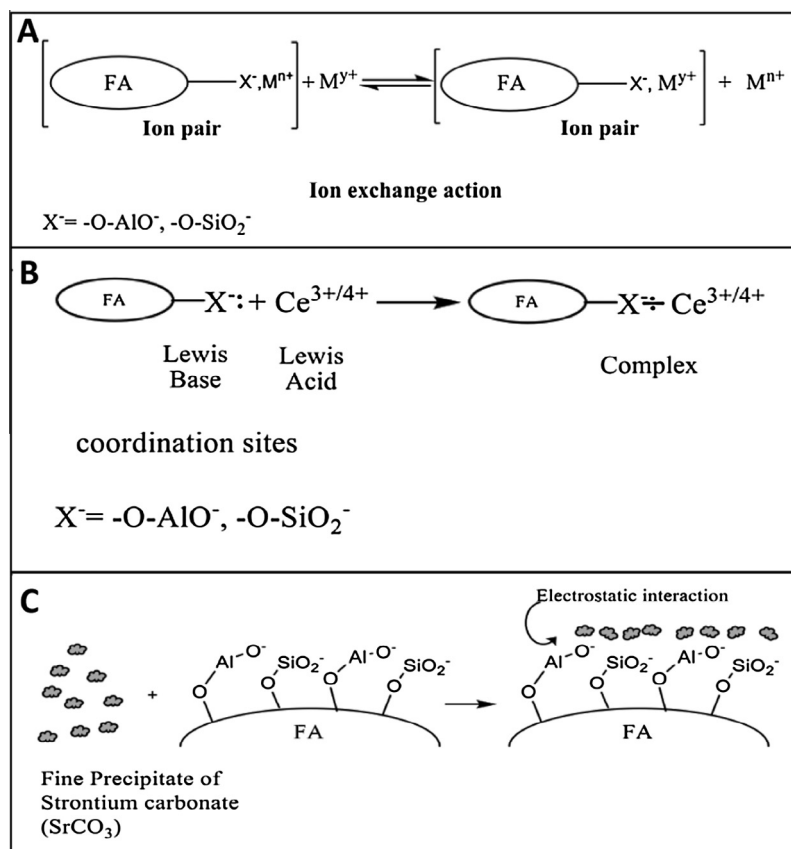
The Ce<sup>3+/4+</sup> ions, due to their affinity to form complexes (as demonstrated by its rapid equilibrium and precipitation in water with OH<sup>–</sup> ions), are expected to undergo coordinative bonding with the non-bonding electrons of functional groups located at the surface of the FA particles (Fig. 3B):

Finally, as previously reported [45], for both types of FA up to 50% of the initial Ca<sup>2+</sup>, in addition to other cations such as Sr<sup>2+</sup>, leaches out in an acid solution as seen in the current work (Table 4).

As it is conceivable that all the above parameters have an effect on functional groups responsible for the FA fixation process, further experimentation taking these factors into consideration is clearly warranted.

Unsurprisingly, a similar fixation approach for aqueous Sr<sup>2+</sup> was unsuccessful (Table 4) as the high concentration of inherent strontium in the FA (~0.1–0.3 wt.%, Table 1) simply leached out to the bulk solution. In acidic environments, increased amounts of Sr<sup>2+</sup> will leach out, resulting in more available Aluminate and Silicate groups on the surface, contributing to the fixation of Ce<sup>3+/4+</sup>.

Previously [46], the adsorption characteristics of the strontium and cesium nuclides onto kaolinite, a layered silicate mineral, were investigated by batch experiments under various pH conditions and concentrations of groundwater cations. It was reported that the pH exerted a small effect on the adsorption of the ions onto kaolinite while the zeta potential of kaolinite particles showed a negative increase of amphoteric surface charge with increasing pH. Of particular interest was the determination that the adsorption behavior of strontium cations is highly dependent on the concentration of bicarbonate in solution. The thermodynamic saturation index indicated that bicarbonate exerted a great effect



**Fig. 3.** FA fixation mechanisms: (A) cation exchange reagent, (B) coordinative bonding reagent, (C) precipitation of SrCO<sub>3</sub> via the FA at pH > 10.5.

on strontium adsorption by the precipitation of a strontianite (SrCO<sub>3</sub>) and a change in pH.

Utilizing the reported carbonate effect, a new method was developed to avoid this leaching effect of the inherent Sr<sup>2+</sup> from FA. The two approaches attempted, (CO<sub>2(atm)</sub>, Na<sub>2</sub>CO<sub>3(s)</sub>), for increasing the [CO<sub>3</sub><sup>2-</sup>] were found to be equally sufficient to saturate the system and precipitate the Sr<sup>2+</sup> as a carbonate salt. The results indicated (Table 5) that in all the FA experiments no strontium ions are left (within experimental error) in the analyzed extracted solutions. This indicates that all the Sr<sup>2+</sup> ions were precipitated as an insoluble carbonate salt with either an increased diameter >0.45-μm (with the FA acting as a growth catalyst) or alternatively adherence to the FA surface. It is important to state that as Table 5 demonstrated that in the absence of [CO<sub>3</sub><sup>2-</sup>] inherent Sr<sup>2+</sup> undergoes dissolution [Sr]<sub>0</sub> is conceivably higher than the 20 ppm introduced. Therefore, the fact that the ‘real’ fixation concentration under these conditions is higher than [Sr]<sub>0</sub>, along with a negligible detection in the leach solution, demonstrates that FA effectively retains the strontium in this novel method.

In light of the fact that, in the absence of FA, no measurable change in [Sr<sup>2+</sup>] is observed indicates that SrCO<sub>3</sub> is not formed and supports the claim that the SrCO<sub>3</sub> formed is indeed fixed on the surface of the FA. One plausible explanation for the fixation is that the presence of the FA serves as a growth catalyst, generating bigger particles that precipitate more efficiently. Alternatively, as the surface is negatively charged at basic pH, particles with a positive charge will be drawn to the surface of the FA. As it has been reported that the SrCO<sub>3</sub> particles have a positive zeta potential [18,46,47], it is suggested that this is the primary fixation pathway. The electrostatic interaction of the SrCO<sub>3</sub> particles with the FA surface is presented in Fig. 3C. No SrCO<sub>3</sub> could be detected

by the SEM-EDAX analysis, due to the low concentration of Sr<sup>2+</sup> (~10 ppm) in the mother solution.

### 5. Conclusions

The results of this study demonstrate that Class F fly ashes such as SAFA and COFA can potentially serve as a cheap (≤15 \$/ton) partial substitute for the fixation of radioactive nucleotides.

The fixation properties of the fly ash are attributed to the presence of –AlO<sub>2</sub><sup>-</sup> and –SiO<sub>3</sub><sup>-</sup> at the aluminosilicate glassy phase. These groups likely undergo coordinative interactions with Ce<sup>3+/4+</sup> vs. cation exchange interactions with Cs<sup>+</sup>.

A novel method for the utilization of the negatively charged surface of the FA towards the retention of positively charged particles has been developed and its feasibility was demonstrated for SrCO<sub>3</sub>.

The current findings suggest that Class F FA can conceivably retain more than one type of simulant by utilizing multiple fixation mechanisms in parallel (e.g. cation exchange interactions with cesium while precipitating strontium as SrCO<sub>3</sub>).

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.fuel.2015.02.111>.

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