Evaluation of radium and caesium containment performance of palm oil fuel ash-supplemented cementitious backfill for borehole disposal: Kinetic investigations

E Phillip¹,²*, K S Khoo¹, M A W Yusof² and R O Abdel Rahman³

¹Department of Applied Physics, Faculty of Science and Technology, National University of Malaysia (UKM), Bangi, Selangor, Malaysia
²Nuclear Malaysia, Bangi, Selangor, Malaysia
³Hot Lab. Center, Atomic Energy Authority of Egypt, P.O. No. 13759, Cairo, Egypt

*esther@nuclearmalaysia.gov.my

Abstract. Radium and caesium have been identified among the major radionuclides found in disused sealed radioactive sources (DSRSs) and these DSRSs are potentially planned to be disposed in borehole disposal. In borehole disposal, cementitious backfill is commonly used as engineered barrier for containment of radionuclides. Present study evaluates the potential use of palm oil fuel ash (POFA)-supplemented cementitious backfill to contain radium and caesium radionuclides. In this respect, kinetic investigations were carried out to understand the nature of the sorption process onto both Ordinary Portland Cement (OPC) and POFA-supplemented cementitious material. The results showed that the sorption process for both cementitious backfill materials reached equilibrium within 48 hours and 24 hours for radium and caesium, respectively. For both backfill materials, results from kinetic analysis of radium and caesium indicated that the sorption process followed pseudo-second order model thus suggesting chemisorption reaction. Meanwhile, pore diffusion and film diffusion were identified as the main mechanisms controlling the sorption process. It was also found that the sorption capacity was higher for POFA-supplemented cementitious material (6–60 Bq g⁻¹) compared to OPC (1–44 Bq g⁻¹) indicating valuable containment of radium and caesium by POFA-supplemented cementitious backfill.

1. Introduction
Sealed radioactive sources (SRSs) are widely used in numerous applications particularly in medicine, industry and research. In many cases, once the sources decay to a level at which they are no longer applicable, or are damaged to a point where they no longer able to serve their purposes these sources are deemed disused and referred to as disused sealed radioactive sources (DSRSs). Nevertheless, these DSRSs may still potentially caused hazards to humans and the environment thus requires safe and proper management. DSRSs contain a wide array of radionuclides with a broad spectrum of activity and are divided into different categories. For example, categories 3-5 DSRSs include but not limited to industrial gauges, smoke detectors, lightning conductors and Ra needles containing Am-241, Ra-226, Cs-137, Sr-90, Co-60 [13]. Short-lived radionuclides are easily managed by utilizing decay storage meanwhile longer-lived radionuclides in particular Ra-226 require long-term management such as by disposal. Realizing the need for safe, secure and permanent management of DSRSs in its member...
states, the IAEA is actively promoting the implementation of narrow diameter borehole disposal for DSRFs especially for countries without any geological repositories.

The borehole disposal concept adopts a multi-barrier system that encompasses geological and engineered barrier system. The engineered barrier system is basically made up of waste package, waste containers, and backfill. Similar to other disposal concepts, the main purpose of the backfill, that surrounds the waste container, is to limit the release of radionuclide contaminants to the geosphere upon the failure of the waste container[12][15]. In many disposal systems, commonly used backfill materials include soil, rock, clay, bentonite and cement. In borehole disposal, cement has been proposed as the backfill material. Cement and cementitious materials are favored materials to be used. Apart from the physical and mechanical benefits provided these materials also contain different minerals with high sorptivity for many radionuclides to provide for effective radionuclides containment in a longer period[10]. Additionally, the alkaline cement environment makes the radionuclides less soluble and mobile[7]. Thus, retention and retardation of radionuclides migration can be achieved.

Many radionuclides bind strongly to cementitious matrices[3][4][36] and therefore sorption properties can be exploited for containment of radionuclide contaminants. In hardened cement paste, calcium silicate hydrate (C-S-H) (chemical composition: CaO-SiO$_2$-H$_2$O) is the predominant phase responsible for most metals and radionuclides binding[5][21][36]. Pozzolanic reaction that occurs when a supplementary cementitious material (SCM) is added to a cement blend resulted in higher amounts of C-S-H phases as some of the Ca(OH)$_2$ formed during early hydration reacts with Si from the SCM to produce more C-S-H[10].

Various types of cement-based materials of varying SCM are used and proposed as backfill materials to fulfil the physical, mechanical and chemical requirements of the said application, for example, cement containing fly ash and silica fume[17]. Cement containing palm oil fuel ash (POFA) is slowly gaining attention as a green product to support environmental sustainability in the construction field. POFA is a by-product generated from the palm oil processing industry that contains a large amount of silica[34] and has a high potential to be used as cement replacement[35]. Some publications reported the feasibility of using POFA as SCM to enhance the physical and mechanical properties of cement[24][25]. On the other hand, the sorptivity of contaminant by POFA was attributed to its silica-based structure e.g. silanols (Si-OH) and siloxanes (Si-O-Si)[44]. This study is dedicated to demonstrate the potential of POFA-supplemented cementitious material as backfill for radionuclides containment based on their sorption performance compared to the Portland cement backfill. The sorption performance was analyzed from the kinetic point of view. The radionuclides of interest are Ra and Cs; both are major radionuclides found in DSRFs. Many studies have been dedicated to investigating the containment of Cs in cement systems due to its solubility in the high pH environment of the cement-based materials[27][19][2][6]. Despite Ra was reported as the second most important divalent elements (M$^{2+}$) in radioactive waste disposal due to its long half-life that is critical from the environmental perspective[22], yet investigations on Ra retention into cement-based materials are comparatively scarce[36].

2. Experimental

2.1. Materials

The cement used in this study is Ordinary Portland cement (OPC) type CEM I 42.5N manufactured by Tasek Corporation Berhad. The OPC sample was sieved to obtain particles of less than 250 μm prior to its use. POFA sample was collected from Jugra Palm Oil Mill in Banting, Selangor, Malaysia. The chemical compositions of the OPC and POFA were determined using EDXRF (Shimadzu), and the results are listed in Table 1. The POFA sample was subjected to a series of drying, heat-treatment, grinding and sieving processes to obtain the final POFA sample with particles sizes less than 250 μm.
Table 1. Chemical composition of raw materials OPC and POFA.

| Chemical composition | OPC  | POFA |
|----------------------|------|------|
| SiO₂                 | 21%  | 54%  |
| CaO                  | 60%  | 5%   |
| Al₂O₃                | 11%  | 0%   |
| K₂O                  | 2%   | 32%  |
| Fe₂O₃                | 5%   | 4%   |
| P₂O₅                 | 0%   | 5%   |
| SO₃                  | 1%   | 0%   |

Cubes of hardened cement paste were prepared from OPC alone as well as the mixture of OPC and POFA. An optimum mixture design of 30% OPC replacement by POFA and water to cement ratio of 0.4 was used. In this study, one-year-old backfill materials were used, where the backfill cubes were crushed, ground and sieved to obtain powdered samples of less than 250 μm and these samples were used. Meanwhile, cement-equilibrated water was prepared by agitating cementitious materials in distilled water for 28 days followed by decantation.

The solution containing Ra and Cs radionuclides were prepared from Ra-226 and Cs-134 obtained from Eckert & Ziegler. Working solutions of Ra and Cs were 6 Bq mL⁻¹ and 10 Bq mL⁻¹, respectively. All the working solutions were prepared by dilution in cement-equilibrated water; the chemical composition of the pore water solutions for both samples is listed in Table 2. Radioactivity of Ra and Cs was measured using a gamma spectrometer (Canberra). The radioactivity of Ra was detected at energy 186 keV and Cs at 605 keV.

Table 2. Chemical composition of the pore water samples used in the sorption experiments

(a) OPC pore water solution (b) POFA-supplemented cementitious material pore water solution.

| Chemical composition | Cement-equilibrated water (OPC) | Cement-equilibrated water (POFA-supplemented cementitious material) |
|----------------------|----------------------------------|---------------------------------------------------------------|
| Ca                   | 96%                             | 61%                                                          |
| K                    | 3%                              | 13%                                                          |
| Mg                   | 0%                              | 13%                                                          |
| Na                   | 1%                              | 13%                                                          |

2.2. Sorption experiments

Batch sorption experiments were performed to investigate the kinetic sorptive behavior of Ra and Cs onto the cementitious materials (OPC and POFA-supplemented cementitious material). Samples containing radionuclides-pore water solution and the cementitious materials in powdered form at a fixed dosage of 0.1 g mL⁻¹ were continuously agitated, to prevent agglomeration, on an orbital shaker at 150 rpm. Experiments were conducted for periods ranging from 5 mins to 4 days at room temperature (25±2°C). The aliquots were centrifuged at 4000 rpm for 20 minutes to separate the supernatant and precipitate. The radioactivity of the supernatant samples containing unabsorbed Ra and Cs were analyzed using a gamma spectrometer. All experiments were done in triplicates. The amount of sorbed radionuclide per unit mass of sorbent, q (Bq g⁻¹), at any time, t, is given as Equation (1):

\[ q_t = \frac{(c_0-c_t)V}{m} \]  (1)
where,
- $C_0$ is the initial activity concentration of sorbate in the bulk solution (Bq mL$^{-1}$);
- $C_t$ is the activity concentration of sorbate in the bulk solution at time $t$ (Bq mL$^{-1}$);
- $V$ is the volume of the bulk solution (mL);
- $m$ is the mass of the sorbent (g).

2.3. Kinetic analysis models

2.3.1. Pseudo-first-order model. Linearized form of pseudo-first-order model of Lagergren [18] is given as Equation (2):

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t$$  \hspace{1cm} (2)

where,
- $q_e$ is the amount of radionuclide sorbed at equilibrium (Bq g$^{-1}$);
- $q_t$ is the amount of radionuclide sorbed at time $t$ (Bq g$^{-1}$);
- $k_1$ is the equilibrium rate constant of pseudo-first-order sorption (min$^{-1}$);
- $t$ is the time (min).

2.3.2. Pseudo-second-order model. Linear form of the pseudo-second-order model is given as Equation (3):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{a_e} t$$  \hspace{1cm} (3)

where,
- $q_e$ is the amount of radionuclide sorbed at equilibrium (Bq g$^{-1}$);
- $q_t$ is the amount of radionuclide sorbed at time $t$ (Bq g$^{-1}$);
- $k_2$ is the equilibrium rate constant of pseudo-second-order sorption (Bq g$^{-1}$min$^{-1}$).

The values of $q_e$ and $k_2$ were determined from the slope and intercept of the linear plot $t/q_t$ against $t$, respectively. Initial sorption rate, $h$ (Bq g$^{-1}$ min$^{-1}$) is defined as Equation (4):

$$h = \frac{k_2 q_e^2}{a_e}$$  \hspace{1cm} (4)

2.3.3. Elovich’s model. Elovich’s model is used to describe reaction rates that increase exponentially with the adsorption, which implies multilayer sorption[1][3][43]. The model is used to describe different mechanisms, i.e. bulk and surface diffusion, as well as chemisorption. Linearized form [32] of Elovich’s model is given as Equation (5):

$$q_t = \frac{ln a_e b_e}{b_e} + \frac{1}{b_e} ln t$$  \hspace{1cm} (5)

where,
- $q_t$ is the amount of radionuclide sorbed at time $t$ (Bq g$^{-1}$);
- $a_e$ is the initial sorption rate (Bq g$^{-1}$ min$^{-1}$);
- $b_e$ is the desorption constant related to the activation energy for sorption reaction (Bq g$^{-1}$).

2.3.4. Intraparticle diffusion model (IPD). IPD model introduced by Weber and Morris (1963) is widely used in analysing sorption mechanisms[23] and is given as Equation (6):

$$q_t = k_{ipd} t^{1/2} + \theta$$  \hspace{1cm} (6)
where,

- \( q_t \) is the amount of radionuclide sorbed at time \( t \) (Bq g\(^{-1}\));
- \( k_{ipd} \) is the IPD rate constant (Bq g\(^{-1}\) min\(^{1/2}\));
- \( \theta \) is a constant related to the boundary layer thickness (Bq g\(^{-1}\)).

2.3.5. Bangham’s model. Bangham’s model assumes that intraparticle (pore) diffusion is the only rate-controlling step in a sorption process and its equation is expressed as Equation (7):

\[
\log \left[ \log \left( \frac{C_o}{C_o - C_s q_t} \right) \right] = \log \left[ \frac{k_b C_s}{2.303V} \right] + \alpha \log t
\]

where,
- \( C_o \) is the initial activity concentration of the radionuclide (sorbate) (Bq L\(^{-1}\));
- \( C_s \) is the weight of cementitious backfill material (sorbent) used per liter of solution (g L\(^{-1}\));
- \( q_t \) is the amount of radionuclide sorbed at time \( t \) (Bq g\(^{-1}\));
- \( k_b \) is the Bangham’s constant;
- \( \alpha \) is also a constant with value <1.

\( k_b \) and \( \alpha \) were obtained from the intercept and slope of the linear plots of \( \log \left[ \log \left( \frac{C_o}{C_o - C_s q_t} \right) \right] \) against \( \log t \).

2.3.6. Boyd’s model. The outcome from the IPD model was further analysed using the film diffusion model of Boyd’s to determine the actual rate limiting step involved in the sorption process. This model assumes that the main resistance to diffusion is the boundary layer surrounding the adsorbent particle[23]. The Boyd’s model is expressed as Equation (8):

\[
F(t) = 1 - \frac{6}{\pi^2} \exp \left( 1 - B_t \right)
\]

where,
- \( F(t) \) is the fraction of radionuclide sorbed at time \( t \);
- \( B_t \) is the mathematical function of \( F(t) \).

\( F(t) \) is given as Equation (9):

\[
F(t) = \frac{q_t}{q_e}
\]

where,
- \( q_t \) is the amount of radionuclide sorbed at time \( t \) (Bq g\(^{-1}\));
- \( q_e \) is the amount of radionuclide sorbed at equilibrium (Bq g\(^{-1}\)).

The following approximations are used to compute the value of \( B_t \):

For \( F(t) \) values > 0.85, equation (10) is used:

\[
B_t = 0.4977 - \ln \left( 1 - F(t) \right)
\]

For \( F(t) \) values < 0.85, Equation (11) is used:

\[
B_t = \left( \sqrt{\pi} - \sqrt{\pi - \left( \frac{\pi^2 F(t)}{3} \right)} \right)^2
\]
3. Results and discussions

3.1. Effect of contact time
Experimental results showing the effect of contact time on the batch sorption of Ra and Cs onto the cementitious materials are depicted in Figure 1 (a) and (b) respectively. Typical sorption curves depicting the rapid sorption process in the beginning and the slow sorption process that followed were observed for both Ra and Cs. The rapid sorption process could be attributed to the vast availability of active sorption sites at the beginning of the reaction and as sorption progressed more sites become occupied leading to slow sorption that occurred in the longer period until equilibrium was reached [9].

![Figure 1](image_url)

**Figure 1.** Effect of contact time on sorption of radionuclides by cementitious backfill materials: at fixed sorbent dosage, 0.1 g mL\(^{-1}\) at room temperature (25±2°C) (a) Ra with initial activity concentration, 6 Bq mL\(^{-1}\); (b) Cs with initial activity concentration 10 Bq mL\(^{-1}\).

It is also noted that the sorption capacity of Ra and Cs by POFA-supplemented cementitious material is higher than OPC for the entire period investigated thus indicating the contribution of POFA
to the sorption of Ra and Cs. The sorption capacity, given by the values of $q_e$ for Ra sorption by POFA-supplemented cementitious material was in the range of 48 – 60 Bq g$^{-1}$ compared to 24 – 44 Bq g$^{-1}$ for OPC. Meanwhile, the values of $q_e$ for Cs sorption by POFA-supplemented cementitious material ranged from 6 – 24 Bq g$^{-1}$ and for OPC the values of $q_e$ were lower ranging from 1–10 Bq g$^{-1}$. According to [3][21][29][36], radionuclides retention on cement was primarily controlled by C-S-H phases. Ochs et al. [27] specifically pointed out to the role of C-S-H as the main sorbing phase for Cs in hardened cement paste. In this study, it was very likely that the sorption mechanisms involved surface sorption and incorporation of Ra and Cs in the interlayer of C-S-H that might include a substitution of Ca$^{2+}$ [36][37] or complexation on deprotonated silanol groups [15]. The presence of more C-S-H phases due to pozzolanic reaction in the POFA-supplemented cementitious material could have led to the higher sorption capacity of Ra and Cs. Another reason could be due to the presence of free SiO$_2$ from POFA. At high pH, negative surface charge on SiO$_2$ increased and led to a stronger attraction for positive such as Ra and Cs ions. This could also be explained the rapid sorption in the beginning and as the reaction progressed more SiO$_2$ was consumed and hence the gradual and finally steady sorption as interaction with C-S-H dominated. Yusof et al. [44] explained the mechanism of As sorption on POFA via the complexation of SiO$_2$.

It was mentioned that the sorption of alkaline earth metals by cementitious materials are greatly affected by the presence of Ca [24] as well as other alkalis (such as Na and K), where these cations decreased the sorption of other divalent ions on C-S-H [21]. The sorption process for both samples reached equilibrium within 48 hours and 24 hours for Ra and Cs, respectively. In comparison to findings by Volchek et al. [38] that investigated the sorption of Cs by Portland cement mortar coupons, the equilibrium in our study was achieved much earlier.

In order to elucidate the sorption mechanism, several kinetic models were tested using the experimental data. Kinetic models, namely pseudo-first order, pseudo-second order, Elovich’s, IPD, Bangham’s and Boyd’s models, were used to investigate the reaction rates and controlling sorption mechanisms between the radio-contaminants (Ra and Cs) and the proposed cementitious backfill materials.

### 3.2. Determination of reaction rates

#### 3.2.1. Pseudo-first order model.

Pseudo-first order model illustrated by linear plots of log ($q_e$-$q_t$) against $t$ gave the values of $q_e$ from the intercept and $k_1$ from the slope as well as the values for correlation coefficient, $R^2$. The parameter values are shown in Table 3. It was observed that the values of $q_e$ calculated were inconsistent with those obtained experimentally. Moreover, it was also observed that the model was valid only during the early phase of the sorption process for Cs sorption similar to findings reported by[3][9][11][38]. Subsequently, the use of this model to represent the reaction kinetics throughout the reaction time would lead to underestimating the value of sorbed radionuclides. Therefore, the model was deemed unsuitable to be used for prediction of Ra and Cs sorption for the entire sorption period.

#### 3.2.2. Pseudo-second-order model. As the sorption data was not successfully applied using the pseudo-first order model, it was further treated with pseudo-second order model. This model assumes that the uptake rate is second order with respect to the available sites[11]. Pseudo-second order model is depicted in Figure 2 (a) and (b) as plot of $t/q_e$ against $t$ and the fitting parameter values are shown in Table 3. The high correlation coefficient, $R^2$, values ($R^2=1$) and comparable experimental and calculated $q_e$ values suggested that the sorption process could be well explained by this model. The findings also proposed that the rate limiting step for the sorption process was chemisorption that involved valency forces through sharing of electrons between sorbent and sorbate or covalent forces from exchange of electrons between sorbent and sorbate [11]. Similar findings were obtained by Volchek et al.[38].
The equilibrium rate constant of pseudo-second-order sorption, $k_2$, values obtained for OPC (Ra: 1.52E-03 Bq g$^{-1}$ min$^{-1}$; Cs: 1.83E-03 Bq g$^{-1}$ min$^{-1}$) were higher than that of POFA-supplemented cementitious material (Ra: 1.41E-03 Bq g$^{-1}$ min$^{-1}$; Cs: 6.38E-04 Bq g$^{-1}$ min$^{-1}$). However, the value for Ra sorption by OPC was just slightly higher compared to POFA-supplemented cementitious material. The initial sorption rate, $h$, values were higher for sorption by POFA-supplemented cementitious materials (Ra: 5.13E+00 Bq g$^{-1}$ min$^{-1}$; Cs: 1.96E-01 Bq g$^{-1}$ min$^{-1}$) than OPC (Ra: 2.65E+00 Bq g$^{-1}$ min$^{-1}$; Cs: 1.96E-01 Bq g$^{-2}$ min$^{-1}$) indicating rapid initial sorption by POFA-supplemented cementitious materials.

![Figure 2](image_url)

**Figure 2.** Pseudo-second-order model for the sorption of radio-contaminants by OPC and POFA-supplemented cementitious materials (a) Ra (b) Cs.

### 3.2.3. Elovich’s model

The initial sorption rate, $a_e$, and the desorption constant, $b_o$, were calculated from the intercept and slope of the linear Elovich’s plot $q_e$ against $\ln t$. The results obtained were
presented in Figure 3 (a) and (b) and Table 3. A linear trend was noted for the fast sorption then the data deviated, which implied that the sorption in the fast period proceeded via exponential coverage on the surface[1][3]. The good correlation coefficient, $R^2$, values obtained indicated the applicability of this model to the sorption of Ra and Cs. Nevertheless, it was noticed that the model suited sorption by POFA-supplemented cementitious material ($R^2= 0.95 – 0.98$) better than the OPC ($R^2=0.81 – 0.92$). It was also observed that the sorption was more rapid for POFA-supplemented cementitious material (Ra:1.24E+10 Bq g$^{-1}$ min$^{-1}$; Cs:2.27E+00 Bq g$^{-1}$ min$^{-1}$) compared to the OPC (Ra: 2.67E+04 Bq g$^{-1}$ min$^{-1}$; Cs: 1.95E+00 Bq g$^{-1}$ min$^{-1}$). It was also observed that the $b_e$ values for Ra was higher for POFA-supplemented cementitious material (5.11E-01 Bq g$^{-1}$) compared to the OPC (3.95E-01 Bq g$^{-1}$). However, the $b_e$ values for Cs was higher for OPC (7.67E-01 Bq g$^{-1}$) in comparison to the POFA-supplemented cementitious material (3.06E-01 Bq g$^{-1}$).

Figure 3. Elovich’s model for the sorption of radio-contaminants by OPC and POFA-supplemented cementitious materials (a) Ra (b) Cs.
Table 3. Kinetic parameters obtained from various models.

| Rate model          | Parameter | OPC (Ra) | OPC (Cs) | POFA-supplemented cementitious material (Ra) | POFA-supplemented cementitious material (Cs) |
|---------------------|-----------|----------|----------|---------------------------------------------|---------------------------------------------|
|                     |           | Ra       | Cs       | Ra                                          | Cs                                          |
| Pseudo-first order  | $k_1$ (min$^{-1}$) | 9.21E-04 | 4.61E-03 | 1.61E-03                                   | 2.53E-03                                   |
|                     | $q_e$ (Bq g$^{-1}$) | 1.23E+01 | 5.45E+00 | 9.69E+00                                   | 1.59E+01                                   |
|                     | $R^2$     | 0.79     | 0.90     | 0.95                                        | 0.95                                        |
| Pseudo-second order | $k_2$ (Bq g$^{-1}$ min$^{-1}$) | 1.52E-03 | 1.83E-03 | 1.41E-03                                   | 6.38E-04                                   |
|                     | $q_e$ (Bq g$^{-1}$) | 4.18E+01 | 1.03E+01 | 6.02E+01                                   | 2.40E+01                                   |
|                     | $R^2$     | 4.46E+01 | 9.87E+00 | 6.01E+01                                   | 2.39E+01                                   |
|                     | $q_e$ (Bq g$^{-1}$) (Experimental) | 2.65E+00 | 1.96E-01 | 5.13E+00                                   | 3.67E-01                                   |
|                     | $R^2$     | 1.00     | 1.00     | 1.00                                        | 1.00                                        |
| Elovich’s           | $a_e$ (Bq g$^{-1}$ min$^{-1}$) | 2.67E+04 | 1.95E+00 | 1.24E+10                                   | 2.27E+00                                   |
|                     | $b_e$ (Bq g$^{-1}$) | 3.95E-01 | 7.67E-01 | 5.11E-01                                   | 3.06E-01                                   |
|                     | $R^2$     | 0.92     | 0.81     | 0.98                                        | 0.95                                        |

3.3. Controlling sorption mechanism

3.3.1. Intraparticle diffusion model (IPD). IPD model is illustrated by plot of $q_t$ against $t^{1/2}$ (Figure 4 (a) and (b)) that gives the value of $k_{ipd}$ from the slope and $\theta$ from the intercept. The $k_{ipd}$ and $\theta$ values listed in Table 4 referred to the results obtained for the entire contact time investigated. However, it was noted that the results illustrated in (Figure 4 (a) and (b)) showed multi-linear plots instead of a single linear plot that passed through the origin indicating that the sorption processes were controlled by multiple mechanisms[40]. Therefore, the mechanism involved was not limited to pore diffusion alone but could also by other mechanism such as film diffusion. The plots obtained could be divided into three distinct linear regions; each representing a controlling mechanism or several simultaneous controlling mechanisms[33]. The first distinct region that occurred during the initial sorption process demonstrated external diffusion through the boundaries that involved rapid transportation of radionuclides from the liquid phase to the solid boundary of the cementitious materials. This model assumes that external resistance to mass transfer (film diffusion) is only significant during the early stage of a sorption process[23]. The second region was attributed to IPD and the final region illustrates the equilibrium stage in which sorption took place slowly as the surface coverage approached saturation.

It was noticed that the boundary layer thickness increased as sorption progressed indicating large film diffusion resistance.
3.3.2. **Bangham’s model.** Bangham’s model is described by plotting the values of $\log \left[ \log \left( \frac{C_0 - C_t}{C_0 - C_f} \right) \right]$ against $\log t$. Results obtained are tabulated in Table 4. A desired linear fit was however not obtained for the double logarithmic plots as shown by the correlation coefficients, $R^2$, ($R^2 = 0.82 – 0.96$) thus indicating that the sorption kinetics were not limited to only pore diffusion.

3.3.3. **Boyd’s model.** Boyd’s model is demonstrated by plot of $B_t$ against $t$ (Figure 5 (a, b)). The value of $q_e$ used is obtained from the data fitting using pseudo-second order model similar to the approach adopted by Malash et al.[23].

The linear plots obtained did not pass through the origin thus indicated that the rate limiting step for the sorption process was governed by film diffusion (external mass transfer) or chemical reaction [9][16][30].
Figure 5. Boyd’s model for the sorption of radio-contaminants by OPC and POFA-supplemented cementitious materials (a) Ra, (b) Cs.

Table 4. Mechanistic parameters obtained from various models.

| Mechanistic model  | Parameter | OPC      | POFA-supplemented cementitious material |
|--------------------|-----------|----------|-----------------------------------------|
|                    |           | Ra       | Cs                                      | Ra          | Cs          |
| Intra particle diffusion | $k_{ipd}$ (Bq g$^{-1}$ min$^{1/2}$) | 2.12E-01 | 1.27E-01 | 1.69E-01 | 3.43E-01 |
|                     | $\theta$ (Bq g$^{-1}$) | 3.12E+01 | 4.68E+00 | 5.01E+01 | 8.72E+00 |
|                     | $R^2$     | 0.71     | 0.60    | 0.80    | 0.82    |
| Bangham's           | $k_b$     | 1.00E-04 | 1.00E-04 | 3.00E-04 | 4.00E-04 |
|                     | $\alpha$  | 1.17E-01 | 1.14E-01 | 1.11E-01 | 2.11E-01 |
|                     | $R^2$     | 0.93     | 0.82    | 0.96    | 0.93    |
4. Conclusion
The kinetic of Ra and Cs sorption by POFA-supplemented cementitious material was demonstrated and compared with OPC. For Ra, sorption equilibrium was achieved after 48 hours. Meanwhile, for Cs, equilibrium was reached after 24 hours. Ra showed higher sorption by both cementitious materials in comparison to Cs. The sorption capacity of Ra ranged from 24 – 60 Bq g⁻¹ for both cementitious materials. Meanwhile, the sorption capacity of Cs ranging from 1 – 24 Bq g⁻¹ showed much lower values compared to Ra. The sorption capacity by POFA-supplemented cementitious material also exhibited higher values with approximately 5 – 25 Bq g⁻¹ more for POFA-supplemented cementitious material compared to OPC for both Ra and Cs thus indicating additional sorption by C-S-H phases resulted from pozzolanic reaction when POFA was added as SCM. Of the kinetic models applied, pseudo-second order model best described the kinetic data suggesting chemisorption reaction. IPD model and Bangham’s model suggested that pore diffusion mechanism was not the only rate limiting step that controlled the sorption. Furthermore, Boyd’s model suggested that other mechanism such as film diffusion might also occur.

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