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Research Paper

Adsorption behaviour of simulant radionuclide cations and anions in metakaolin-based geopolymer

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HIGHLIGHTS

- Metakaolin-based geopolymers have a permanent charge.
- Ion exchange is the main mechanism for uptake of cationic radionuclides by the geopolymers.
- An ion-exchange thermodynamic model successfully predicts the geopolymer binding of Cs^+ and Sr^{2+}.
- Geopolymer has limited capacity to bind anionic radionuclides.

GRAPHICAL ABSTRACT
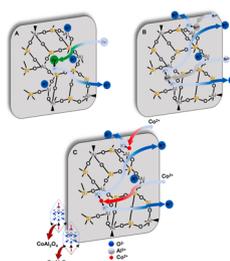
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ABSTRACT

Geopolymers are a class of alkaline-activated materials that have been considered as promising materials for radioactive waste disposal. Currently, metakaolin-based geopolymers (MK-GPs) are attracting interest for the immobilisation of radionuclides in contaminated water from the Fukushima Daiichi Nuclear Power Station. However, the associated chemical interaction mechanisms and the theoretical prediction of the adsorption behaviour of MK-GP in response to cationic radionuclides have not been thoroughly studied or fully understood. In addition, there is a lack of studies on the adsorption capacity of MK-GP for anionic radionuclides. In this study, two types of metakaolin-based (Metastar501 and Sobueclay) geopolymers were synthesised at a $K_2O:SiO_2:H_2O$ ratio of 1:1:13. The binding capacity and interaction mechanism of MK-GP with Cs^+, Sr^{2+}, Co^{2+}, I^-, IO_3^-, SeO_3^{2-}, and SeO_4^{2-} were evaluated based on the zeta potential, radionuclide binding, and alkali leaching. The results showed that MK-GP does not have the ability to incorporate anionic radionuclides irrespective of the metakaolin source used, but both types of geopolymers have a high capacity to immobilise cationic radionuclides. The uptake of Cs^+ was observed as a one-to-one exchange between Cs^+ and K^+ whereas both one–two and one–one ion exchanges are possible in the case of Sr^{2+} and Co^{2+} with K^+. The formation of cobalt blue ($CoAl_2O_4$) also contributed to the binding of Co^{2+}. Thermodynamic modelling was conducted according to the ion exchange mechanism which predicts the binding of Cs^+ and Sr^{2+} at low concentrations.

1. Introduction

The contamination of cooling water with radionuclides and the radioactive waste generated from water is a serious concern in the decommissioning process of the Fukushima Daiichi Nuclear Power Station (FDNPS) (TEPCO, 2013; TEPCO, n.d.). The Tokyo Electric Power Company (TEPCO) has been removing radionuclides from cooling water with several types of adsorbents and plans to safely store the generated radioactive waste for a long time. Selection of the most suitable host material, with high solidification and immobilisation capacity for radioactive waste, is necessary for safe disposal. Moreover, the sealing materials should have low aqueous solubility and should provide stable phases for radionuclides immobilisation (IAEA, 2003; Ojovan and Lee, 2010). Cement-based materials have been considered to solidify and encapsulate radioactive waste for a long time owing to their low cost and high durability (García-Gutiérrez et al., 2018; Koľátková et al., 2017; Bar-Nes et al., 2008). Although cement-based materials show a good immobilisation capacity for some radionuclides, their incompatibilities with several other radionuclides and high free water content, which may cause problematic hydrogen generation, limit their usage in some applications (Volchek et al., 2011; Arbel Haddad et al., 2017; Cornell, 1993). Moreover, high CO_2 emissions and high-energy consumption are unavoidable during the Portland cement manufacturing process (Chen et al., 2015). Therefore, it is important to develop an environmentally friendly solidification material for safe disposal and environmental remediation of nuclear waste.

Geopolymer materials are a class of alkaline-activated materials that can be produced from a chemical process of depolymerisation, polycondensation, and gel networking of an aluminosilicate part commonly referred to as 'precursor' in strong alkaline solution or the activator (Duxson et al., 2007; Provis and Bernal, 2014). Recently, geopolymers have attracted attention as alternative materials for traditional Portland cement in concrete (Shi et al., 2019). Compared with cement-based materials, geopolymers can have superior chemical durability characteristics which are often attributed to their increased degree of silicate polymerisation (Huang and Han, 2011; Li et al., 2013). Since geopolymers have a three-dimensional framework structure of oxygen-linked silicon and aluminium, the negative charge associated with the tetrahedral Al sites is typically balanced by alkali cations, including Na^+ or K^+ from the activator. A geopolymer can also be regarded as a disordered pseudo-zeolite (Huang and Han, 2011; Palomo et al., 2004). There are active sites on the surface of geopolymers owing to the presence of metal oxide groups and thus, they have increased potential in adsorbing heavy metal ions (Ji and Pei, 2019; Siyal et al., 2018). The types of precursors, water/solid ratio, Si/Al ratio, alkalinity of alkali activation solution, and the curing temperature affect the geopolymerisation and could influence the adsorption property (Duxson et al., 2005; Borai et al., 2009).

The use of geopolymers for the proposal of radioactive waste disposal facilities has been considered in industrialised countries (Vance and

Perera, 2009; Xu et al., 2014; Hanzlíček et al., 2006). Metakaolin-based geopolymers (MK-GPs) have been proven to have a high ability to incorporate heavy metal ions through ion exchange (Siyal et al., 2018). The Langmuir model has been used to describe the adsorption behaviour of MK-GP for heavy metals and shows that there are multiple types of binding sites on the surface of MK-GP that can immobilise different types of heavy metals (López et al., 2014). Cs^+ and Sr^{2+} are the most common radionuclides investigated in geopolymer wasteform studies and have been investigated for many years (Kuenzel et al., 2015; Tian and Sasaki, 2019a; Vandevenne et al., 2018). Furthermore, some other radionuclide cations, including Pb, Cu, Cd, Th, U, and Ca, existing in radioactive wastewater can be incorporated into geopolymers (Walkley et al., 2020; El-Eswed et al., 2017). Currently, MK-GP is considered a potential material to solidify waste from FDNPS. However, there are few studies on the immobilisation of Cs^+, Sr^{2+}, and Co^{2+}, which is also a high-content cationic radionuclide from the FDNPS accident (Zhu et al., 2014), in the MK-GP (Siyal et al., 2018). Most studies on the immobilisation capacity of geopolymers for Cs^+ and Sr^{2+} have mainly focused on the confirmation of incorporation, and the associated mechanisms are limited (Kuenzel et al., 2015; Li et al., 2013; Walkley et al., 2020; Vandevenne et al., 2018; El-Kamash et al., 2006; Arbel Haddad et al., 2017). On the other hand, understanding the interaction of MK-GP with anionic radionuclides, including I^-, IO_3^-, SeO_3^{2-}, and SeO_4^{2-} is urgent and important, but this has rarely been discussed in previous studies. In addition, there is limited geochemical modelling studies in the geopolymer system compared with cementitious materials (Gomez-Zamorano et al., 2017; Williamson et al., 2020). Moreover, to the best of authors knowledge, the thermodynamic data on ion-exchange reactions in metakaolin-based geopolymer is still missing. Therefore, it is of great significance to explore and evaluate the potential ability of MK-GP to incorporate both cationic and anionic radionuclides. In this context, the main purpose of this study was to analyse the immobilisation capacity of MK-GP for both cationic radionuclides (Cs^+, Sr^{2+}, and Co^{2+}) and anionic radionuclides (I^-, IO_3^-, SeO_3^{2-}, and SeO_4^{2-}). The zeta potential, binding of radionuclides, and leaching of alkalis were used to evaluate the uptake mechanism. Finally, a thermodynamic model was used to predict the binding of Cs^+ and Sr^{2+} in the geopolymer.

2. Materials and methods

2.1. Materials and geopolymer preparation

Metakaolin from IMERYS-Metastar (hereafter referred to as MS) and Sobueclay, Japan (hereafter SC) were used to prepare the geopolymer, and the average particle size of the metakaolin was 2194.9 nm and 577.4 nm representatively for Metastar and Sobueclay. The chemical composition of metakaolin determined by X-ray fluorescence (XRF) is listed in Table 1, and the ratios of $SiO_2:Al_2O_3$ of MS and SC were 1.04 and 1.01 respectively. A potassium silicate alkali solution was used as an activator for the synthesis of geopolymers. The solutions of the composition $SiO_2/K_2O = R$ (R = 1.0 and 2.1) and $H_2O/K_2O = 11$ and 13 were prepared by mixing an aqueous potassium silicate solution (WAKO, originally containing 29.1 wt% SiO_2, 21.9 wt% K_2O, 49.0 wt% H_2O) into potassium hydroxide solutions of the required concentration until the solution become homogenous and clear. Potassium hydroxide solutions were prepared by dissolving KOH (WAKO 85 wt% KOH) in ultrapure water. The prepared solutions were stored in a laboratory environment (20 °C and RH ≈ 60%) for 24 h to allow equilibration in the solution. The alkaline solutions used for the synthesis of the geopolymer samples are thus defined as $K_2O: SiO_2: H_2O$ (molar ratio) 1:1:11, 1:1:13, 1:2.1:11.7, and 1:2.1:13. Geopolymer samples were prepared by mechanically mixing stoichiometric amounts of metakaolin (Metastar/Sobueclay) with a sufficient quantity of alkaline silicate solution to give $Al_2O_3/K_2O = 1$. The mixture was kneaded for 15 min to form a homogeneous slurry followed by an additional 15 min of vibration to remove entrained air before sealing into a mould (Duxson et al., 2005). The

Table 1
Chemical composition (wt%) of the MS-metakaolin and SC-metakaolin, as determined by X-ray fluorescence.

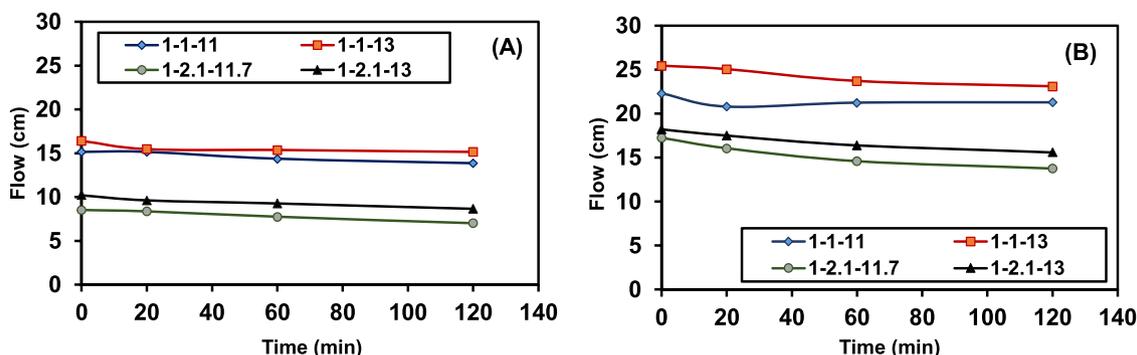| Component	MS-Metakaolin	SC-Metakaolin
SiO_2	52.54	48.59
Al_2O_3	44.81	43.11
Fe_2O_3	0.38	0.54
CaO	0.04	0.21
MgO	4.03	3.66
Na_2O	2.69	2.25
K_2O	0.12	0.13
TiO_2	0.79	1.27
P_2O_5	0.48	1.08
L.O.I.[a]	0.49	1.74

[a] L.O.I. is loss of ignition at 1100 °C for 12 h.

Fig. 1. Slump flow diameters with time for (A) MK-based and (B) SC-based geopolymers (the ratios indicated in the figure legends are K$_2$O:SiO$_2$: H$_2$O).
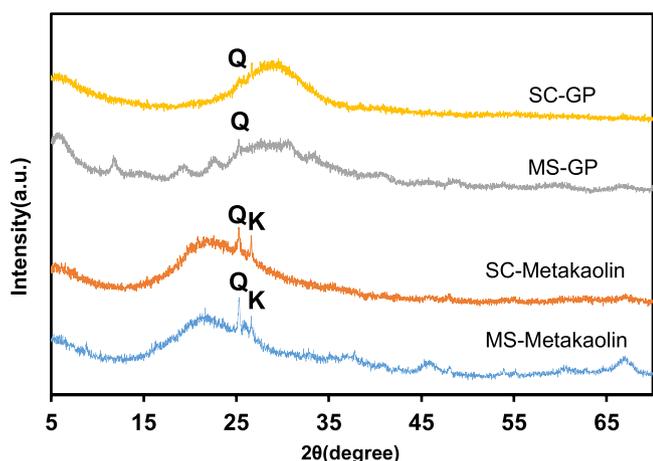

Fig. 2. X-ray diffraction (XRD) patterns for MS and SC metakaolin and their geopolymers.

geopolymer slurry was sealed and cured at 40 °C for 28 days. Subsequently, the hardened geopolymer was demoulded and ground to powder with particle sizes less than 150 μm, and the powder particles were cured for another 3 days at 40 °C before the experiments.

2.2. Experimental procedure

The slump flow experiment specified in JASS15M-103 (which used a cylindrical Φ50 mm× H50 mm mould) was conducted at four different composition ratios (1:1:11, 1:1:13, 1:2.1:11.7, and 1:2.1:13) to select the most suitable composition for the alkaline activator, while achieving a high workability of the geopolymer to meet the requirements for large-scale wasteform production. The slump flow value was measured at 0,

20, 60, and 120 min after mixing. The synthesised geopolymers were characterised by a Rigaku X-ray diffractometer with CuKα radiation, and the measurement conditions were a tube voltage of 40 kV, scanning range of 5–70° 2θ, step size of 0.02° 2θ, and scan speed of 6.5°/min.

A geopolymer suspension with a solid to liquid ratio of 1 g/L was prepared for zeta potential measurements using a zeta potential and particle size analyser apparatus (ELSZ-1000ZS). The zeta potential of the geopolymer was determined in the presence of CsNO$_3$, Sr(NO$_3$)$_2$, Co(NO$_3$)$_2$, KI, KIO$_3$, K$_2$SeO$_3$, and K$_2$SeO$_4$ solutions with ionic strengths of 10 and 100 mmol/L. In each case, KNO$_3$ solution was selected to adjust the ionic strength, whereas KOH was used to adjust the pH., To determine the equilibrium time for the adsorption of ions on geopolymer, the geopolymer was equilibrated with 2 and 4 mmol/L of CsNO$_3$, Sr(NO$_3$)$_2$ or Co(NO$_3$)$_2$ solutions (0.05 g geopolymer powder per 50 mL solution). The solution was filtered with the use of a syringe filter (φ = 0.45 μm) after 1, 3, 5, 7, and 14 d of immersion time, and the concentrations of dissolved ions were measured using inductively coupled plasma-mass spectroscopy (ICP-MS, iCap Q ICP-MS, Thermo Scientific, USA, detection limit 0.01–10 ppb). Batch experiments were performed with CsNO$_3$, Sr(NO$_3$)$_2$, Co(NO$_3$)$_2$, KI, KIO$_3$, K$_2$SeO$_3$, and K$_2$SeO$_4$ solutions at 0.1, 1, 3, 5, and 10 mmol/L with a solid-to-liquid ratio of 1 g/L. After equilibration for 7 d, the liquid phase was filtered with a 0.45 μm syringe filter. The concentrations of the target ion and K$^+$ in the filtered solution were measured by ICP-MS. The amount of bound target ions and leached K$^+$ were calculated by Eqs. 1 and 2:

$$A_b = (C_i - C_t)/R \tag{1}$$

$$A_l = (C_k - C_{pH})/R \tag{2}$$

where A_b is the binding amount of the target ion (mmol/g), R is the solid to liquid ratio (g/L), C_i is the initial concentration (mmol/L), C_t is the concentration of the target ion (mmol/L), A_l is the amount of leached K$^+$ (mmol/g), C_k is the concentration of K$^+$ at time t (mmol/L), and C_{pH}
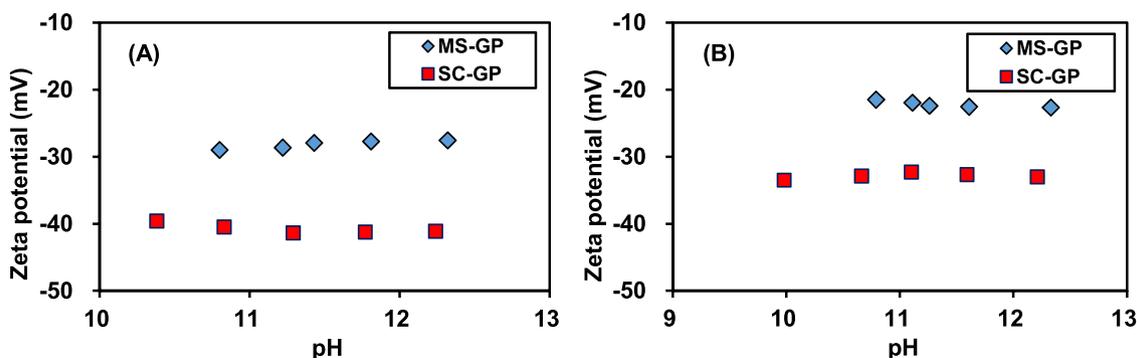

Fig. 3. Zeta potential of geopolymer as a function of pH at the ionic strengths of (A) 10 mmol/L, (B) 100 mmol/L (MS-GP: Metastar metakaolin based geopolymer, SC-GP: Sobue clay metakaolin based geopolymer).
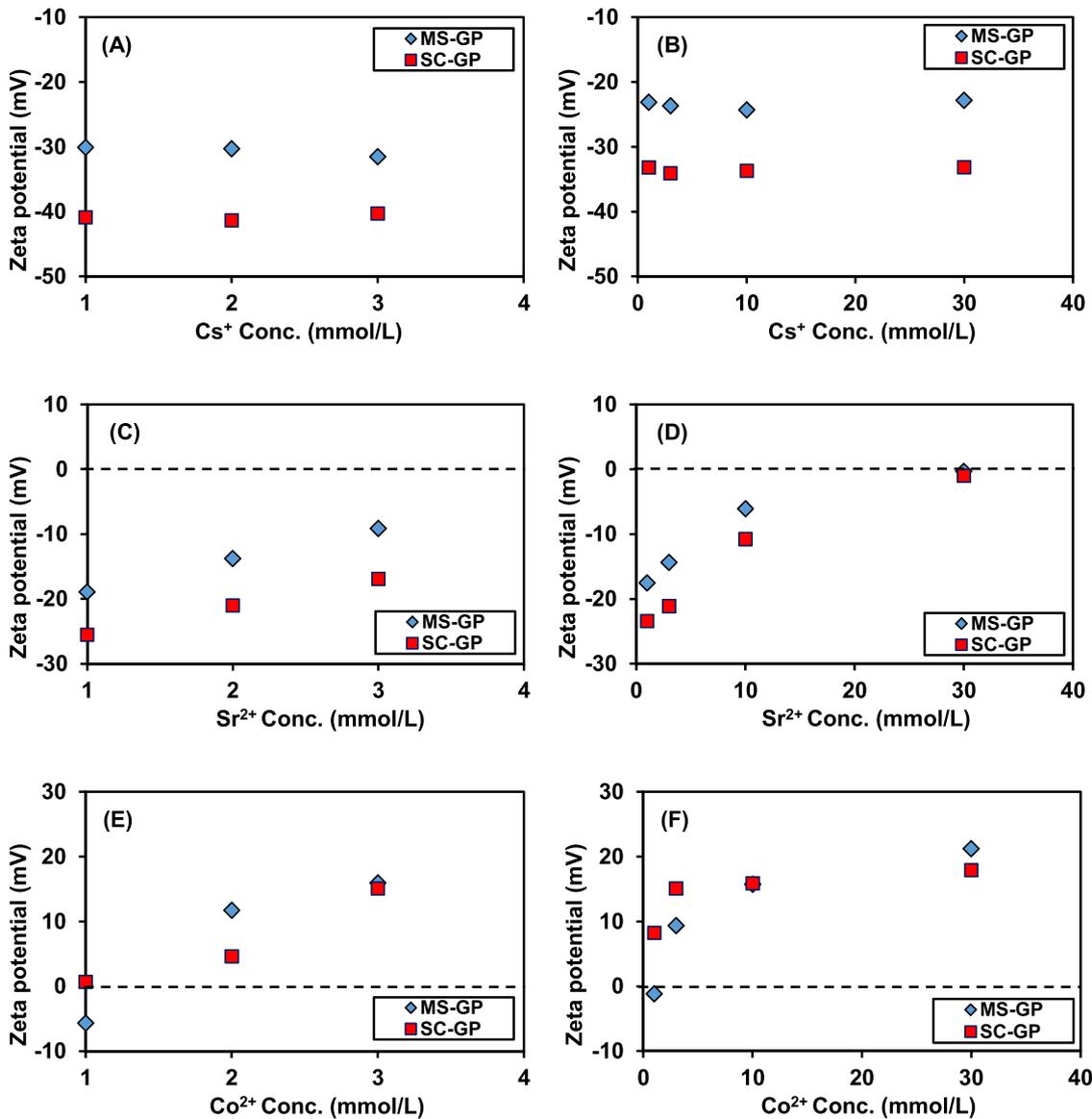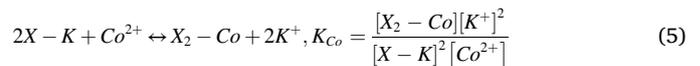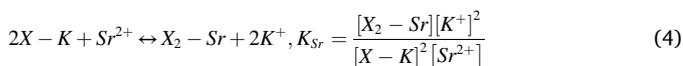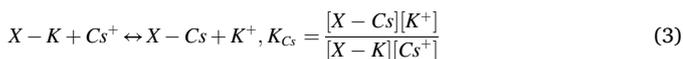
Fig. 4. Zeta potential of geopolymer suspension in (A) Cs$^+$ solution with an ionic strength of 10 mmol/L, (B) Cs$^+$ solution with an ionic strength of 100 mmol/L, (C) Sr^{2+} solution with an ionic strength of 10 mmol/L, (D) Sr^{2+} solution with an ionic strength of 100 mmol/L, (E) Co^{2+} solution with an ionic strength of 10 mmol/L, and (F) Co^{2+} solution with an ionic strength of 100 mmol/L.

is the leached K$^+$ concentration in the blank solution in the absence of radionuclides at the target pH (mmol/L).

2.3. Modelling approach

The ion-exchange model available in the geochemical code PHREEQC was used for ion-exchange reactions between the geopolymer and radionuclide cations (Parkhurst and Appelo, 1999). The activity coefficients were calculated based on the extended Debye–Huckel approach, whose parameters are available in the Phreeqc.dat database. The simulant radionuclides Cs$^+$, Sr^{2+}, and Co^{2+} can be exchanged with the K$^+$ present in the geopolymer as

$$X - K + Cs^+ \leftrightarrow X - Cs + K^+, K_{Cs} = \frac{[X - Cs][K^+]}{[X - K][Cs^+]} \tag{3}$$

$$2X - K + Sr^{2+} \leftrightarrow X_2 - Sr + 2K^+, K_{Sr} = \frac{[X_2 - Sr][K^+]^2}{[X - K]^2[Sr^{2+}]} \tag{4}$$

$$2X - K + Co^{2+} \leftrightarrow X_2 - Co + 2K^+, K_{Co} = \frac{[X_2 - Co][K^+]^2}{[X - K]^2[Co^{2+}]} \tag{5}$$

where X is the exchange site, and K_{Cs}, K_{Sr}, and K_{Co} are the exchange coefficients for Cs$^+$, Sr^{2+}, and Co^{2+}, respectively. The model can be implemented in PHREEQC using the keyword data block of EXCHANGE_MASTER_SPECIES, EXCHANGE_SPECIES, and EXCHANGE.

3. Results and discussion

3.1. Characteristics of geopolymer

The workability or flowability of the geopolymers was evaluated by slump flow experiments, as shown in Fig. 1. The flow of the SC-geopolymer was higher than that of the MS-geopolymer. The difference likely to be related to particle size and/ or calcination condition of the metakaolin. Furthermore, an increase in the SiO$_2$ mole fraction in the alkali activator solution decreased the flow due to increased activator viscosity at higher silica content. Based on the slump flow testing,
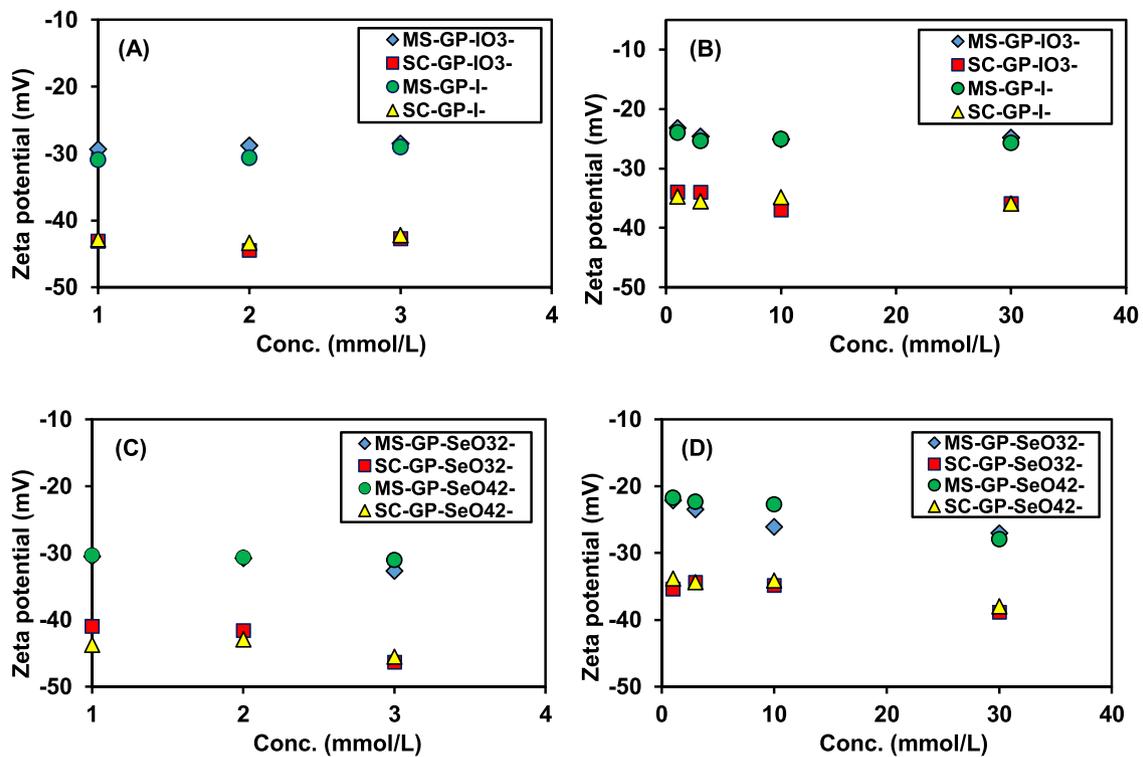
Fig. 5. Zeta potential of geopolymer suspension in (A) I^- or IO_3^- solutions with an ionic strength of 10 mmol/L. (B) I^- or IO_3^- solutions with an ionic strength of 100 mmol/L. (C) SeO_3^{2-} or SeO_4^{2-} solutions with an ionic strength of 10 mmol/L. (D) SeO_3^{2-} or SeO_4^{2-} solution with an ionic strength of 100 mmol/L.
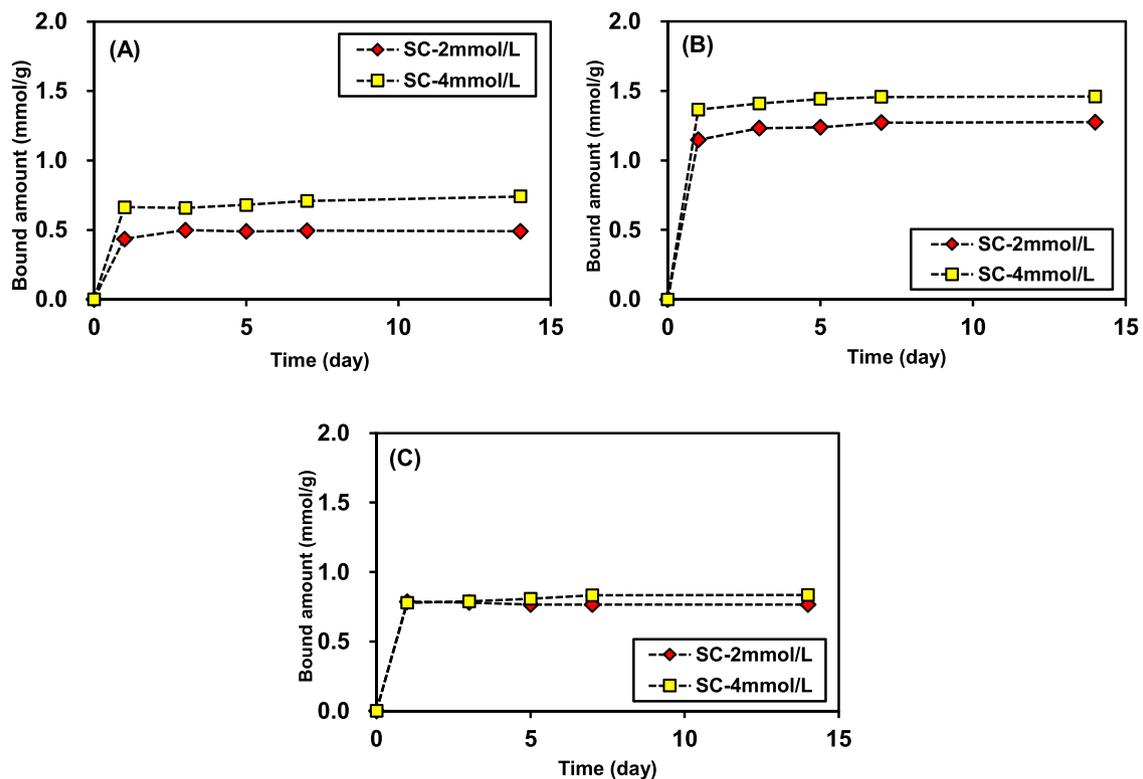
Fig. 6. Binding of (A) Cs^+, (B) Sr^{2+}, and (C) Co^{2+} on SC-geopolymer as a function of time.

the geopolymer with a $K_2O:SiO_2:H_2O$ mole ratio of 1:1:13 had the highest flow and was selected for further analysis in this study.

X-ray diffraction (XRD) measurements were performed to confirm the synthesis of the geopolymer. Fig. 2 shows the XRD patterns of the

metakaolins used for the synthesis and the geopolymer after the synthesis. Both MS and SC metakaolin have structures which are close to amorphous, as reported in previous studies (Kuenzel et al., 2013; Yaru Yang et al., 2021), but the patterns have confirmed the presence of

Fig. 7. Binding of (A) Cs^+, (B) Sr^{2+}, (C) Co^{2+}, (D) I^-, (E) IO_3^-, (F) SeO_3^{2-} and (G) SeO_4^{2-} on geopolymer as a function of concentration.

kaolinite and quartz. Conversely, the XRD patterns of both geopolymers did not show any peaks of kaolinite, but a small amount of quartz remained in the geopolymer. Moreover, the geopolymers yielded a hump in the range of $2\theta = 27-29°$ which indicates amorphous products, and the results are consistent with those reported in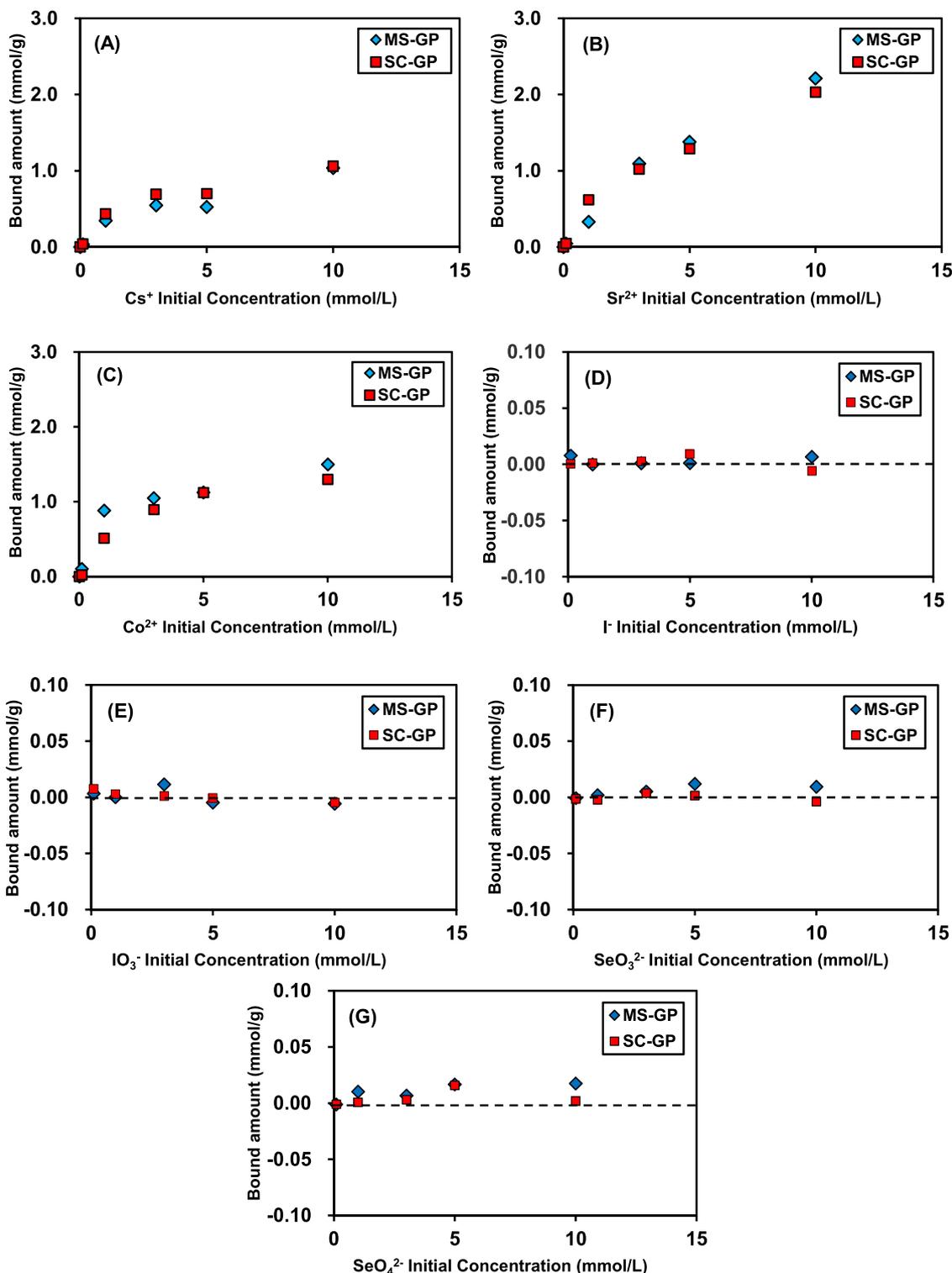 many previous studies on metakaolin (Gualtieri and Bellotto, 1998). Prior to the evaluation of ionic interactions with the geopolymer, the surface electrostatic characteristics were evaluated using zeta potential measurements. It is worth to note that the prepared geopolymer suspension shows

slightly basic pH in water and thus, the alkaline pH was selected for zeta potential experiment. Fig. 3 shows the results of the zeta potential of MS-and SC-based geopolymers in different pH solutions. The zeta potential of the geopolymer is negative and independent of pH, thus indicating the presence of a permanent charge on the surface of the geopolymer which is believed to be derived from the replacement of SiO_4 by AlO_4 in the tetrahedral framework structure (Zhang et al., 2018), and the permanently charged surface can take up cations via electrostatic interactions. The decrease in ionic strength increases the
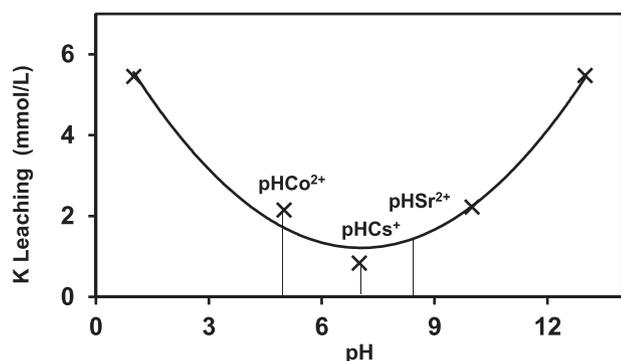
Fig. 8. Leached concentration of K^+ from the geopolymer as a function of pH.

absolute value of the zeta potential due to the formation of a thicker electrical double layer, which is consistent with the results obtained in other studies (Takeya et al., 2020).

3.2. Experimental results on uptake of ions

The measured zeta potential of the geopolymers in the cation-containing solutions are shown in Fig. 4. The effect of Cs^+ concentration on the zeta potential is insignificant compared with that of Sr^{2+} or Co^{2+} solutions, consistent with the differences in the charge states of these respective ions. Moreover, the zeta potential of the geopolymer (for both types of metakaolin) in the Cs^+ solution was nearly equal to the

value obtained for the sample without Cs^+ ions (Fig. 3), thus implying that partial replacement of K^+ by Cs^+ does not contribute to the surface charge variation on the geopolymer. By contrast, the zeta potential of the geopolymer in the Sr^{2+} and Co^{2+} solutions increases towards a positive value, which indicates that the variation in surface charge is caused by the divalent cations. This effect is prominent in the Co^{2+} solution, which shows charge reversal in both geopolymers, even at low concentrations of Co^{2+} ions (Fig. 4(E) and (F)). It should also be noted that a blue precipitate was observed in the geopolymer with Co^{2+} solution, identified as cobalt blue ($CoAl_2O_4$). The effect of cobalt blue formation on the adsorption of Co^{2+} ions on the geopolymer surface needs to be studied in the future, as there are possible competing pathways here, but the formation of cobalt blue does require some degree of extraction of Al from the geopolymer structure and so may have implications for the matrix stability.

The measured zeta potentials in the presence of the anionic radio-nuclide simulant I^-, IO_3^-, SeO_3^{2-}, and SeO_4^{2-} are independent of the anion concentration, and equal to the zeta potential in the blank solution of corresponding pH (Fig. 3). These stable zeta potential results indicate that these ions do not appear to be specifically adsorbed on the surface of the geopolymers (Fig. 5), consistent with the results of other researchers (Al-Mashqbeh et al., 2018).

Before the evaluation of the binding of ions to the geopolymer, the time required to reach equilibrium was determined. The amount of bound Cs^+, Sr^{2+}, and Co^{2+} on the SC-geopolymer as a function of time in solutions with concentrations of 2 and 4 mmol/L is shown in Fig. 6. The results show that the bound amount reached 90% of the total binding in
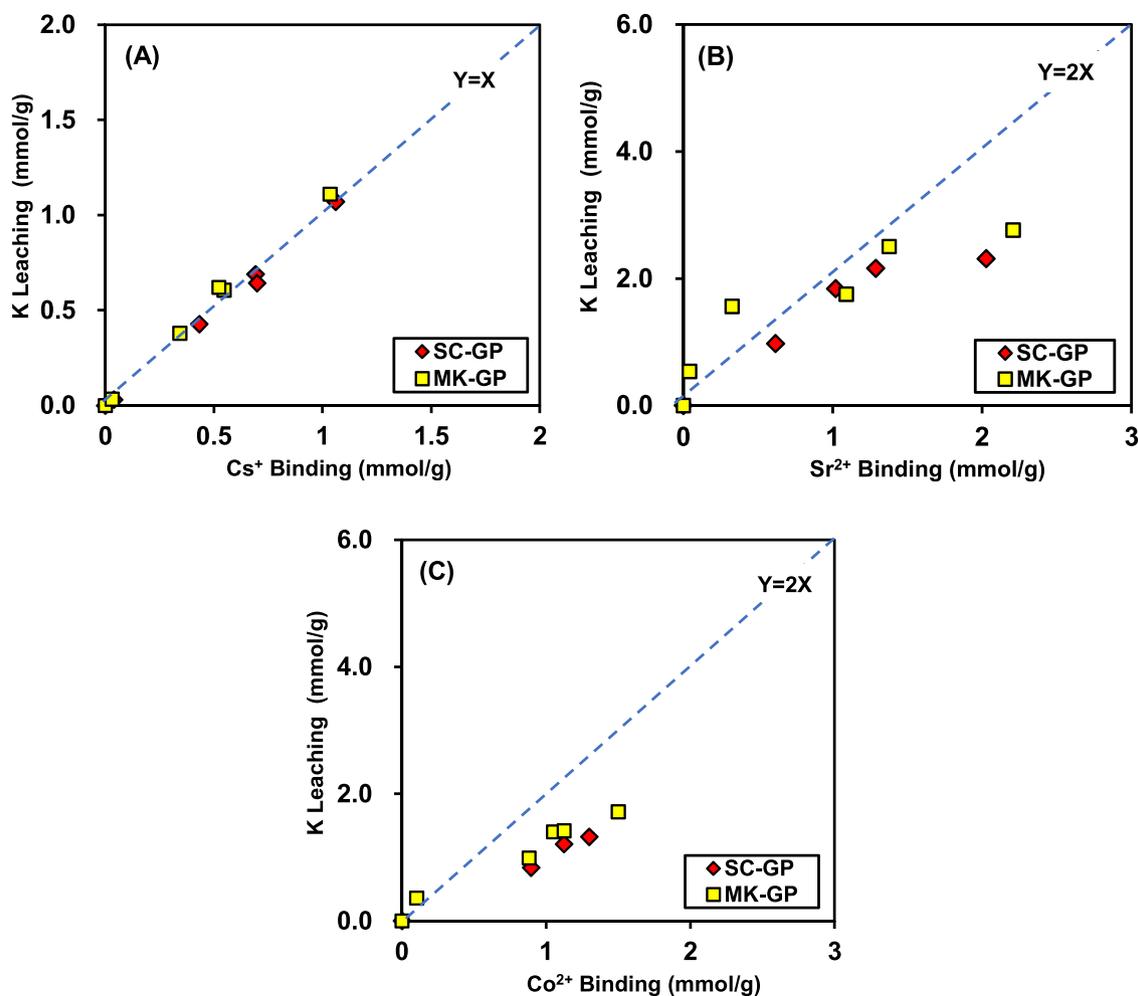

Fig. 9. Relationship between released K^+ and bound cations for geopolymers exposed to (A) Cs^+, (B) Sr^{2+}, and (C) Co^{2+}.
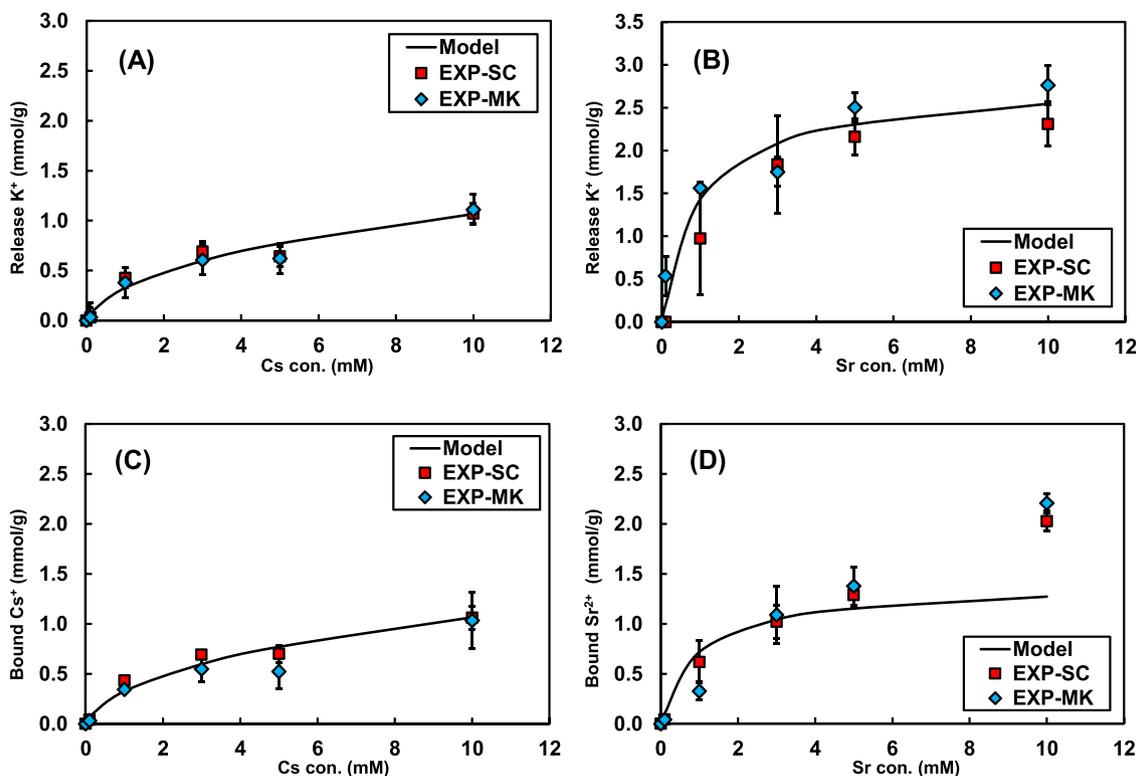
Fig. 10. Fitting of experimental data with modelling results for (A) Cs$^+$ and (B) Sr^{2+}, and the comparison of the predicted and measured (C) Cs$^+$ and (D) Sr^{2+} as a function of concentration.

1 d, and then slowly increased and became constant after 7 d of immersion. Similar results were obtained for each ion in the two solutions (concentrations: 2 or 4 mmol/L). Therefore, 7 d were required to reach an equilibrium of bound ions on the geopolymer, and this is considered as the equilibration time for the binding experiment. The binding of Cs$^+$, Sr^{2+}, and Co^{2+} after equilibrium for 7 d was determined, and the results are shown in Fig. 7 (A), (B) and (C) as a function of concentration for both geopolymers. The total amount of bound cations on the geopolymer increased as a function of concentration, and a higher binding capacity was observed for divalent cations compared with monovalent ions. The maximum concentration of Sr^{2+} (10.0 mmol/L) during the binding experiments was lower than it required for the saturation of Sr (OH)$_2$ (17.8 mmol/L) in the solution, and therefore it is believed that Sr^{2+} was removed from solution only due to binding by the geopolymers. Moreover, the binding capacity of both types of geopolymers for Sr^{2+} was higher than that for Co^{2+}. The type of metakaolin had an insignificant effect on the binding capacity. A similar experiment was conducted on anions, and the results for I$^-$, IO$_3^-$, SeO$_3^{2-}$, and SeO$_4^{2-}$ are shown in Fig. 7 (D), (E) (F)and (G). Regardless of the metakaolin type or the concentration of anions, the geopolymer does not take up any anion from the aqueous solution. This was in good agreement with the zeta potential results (Fig. 5).

The geopolymer releases K$^+$ ions upon the uptake of cations from the aqueous environment, and it is important to understand the mechanisms by which this happens. To determine the K$^+$ (A_l) released in Eq. (2), C_{pH} should be obtained from a batch of control experiments. C_{pH} is the leached concentration of K$^+$ from the geopolymer in the blank solution without simulant radionuclides, and this reflects the washing-out of alkaline pore fluid from the geopolymers during the tests which is not connected to ion exchange processes. Fig. 8 shows that the leaching of K$^+$ from the geopolymer strongly depends on the solution's pH, where acidic and basic solutions enhance the leaching of K$^+$. According to the measured initial pH of each cationic radionuclide solution (as marked in Fig. 8), the values of the parameter C_{pH} were determined to be 2.151,

0.84, and 1.498 mmol/L for Co^{2+}, Cs$^+$, and Sr^{2+}, respectively.

The amounts of leached K$^+$ and bound Cs$^+$, Sr^{2+}, and Co^{2+} can be estimated from the coefficients for each ion and Eqs. (1) and (2), respectively. The relationship between the released K$^+$ and the bound cations is shown in Fig. 9. As shown in Fig. 4, the presence of Cs$^+$ in the solution did not affect the surface charge of the geopolymer. Furthermore, as shown in Fig. 9(A), the leaching amount of K$^+$ was almost equal to the binding amount of Cs$^+$ at each concentration. This indicates a one-to-one ion exchange process taking place between Cs$^+$ and K$^+$. Thus, the main mechanism for Cs$^+$ binding is ion exchange, which is consistent with the results reported in previous studies (Sylvester et al., 2013; Tian and Sasaki, 2019b; Bell et al., 2009). The same approach has been considered for Sr^{2+} and Co^{2+} (where one mole of divalent cation would replace two moles of K$^+$), and the results are shown in Fig. 9(B) and (C). At low concentrations of Sr^{2+}, the uptake of Sr^{2+} is governed by ion exchange although there is some discrepancy at 0.1 and 0.5 mmol/g of Sr^{2+}. However, a higher uptake of Sr^{2+} than the release of stoichiometric K$^+$ was observed at high concentrations, which suggests that another mechanism, in addition to ion exchange, contributes to Sr^{2+} binding in geopolymers. The uptake of Co^{2+} and the release of K$^+$ was lower than that of Sr^{2+} (Fig. 9(C)), and the relationship between the released K$^+$ and bound Co^{2+} was far from the y = 2x line. This implies that the binding mechanism for Co^{2+} in the geopolymer is not dominated by ion exchange, as observed for Cs$^+$ and Sr^{2+}. It is worth to discuss the formation of SrOH$^+$ or CoOH$^+$ ion pair, which can effectively act as a monovalent cation for one-to-one ion exchange (Arcis et al., 2014; Rebecca and Armentrout, 2017). The thermodynamic speciation calculation was performed in PHREEQC under the similar condition as adopted for binding experiment, and it was found that the formation of SrOH$^+$ or CoOH$^+$ was negligible compared to Sr^{2+} or Co^{2+}. Therefore, the deviation of leaching/binding ratio of K$^+$ to Sr^{2+} and Co^{2+} is attributed to charge-unbalanced ion exchange between Sr^{2+} or Co^{2+} and K$^+$ as well as the formation of cobalt blue in the case of Co^{2+} solution. In this study, there was not a significant difference between the two types of
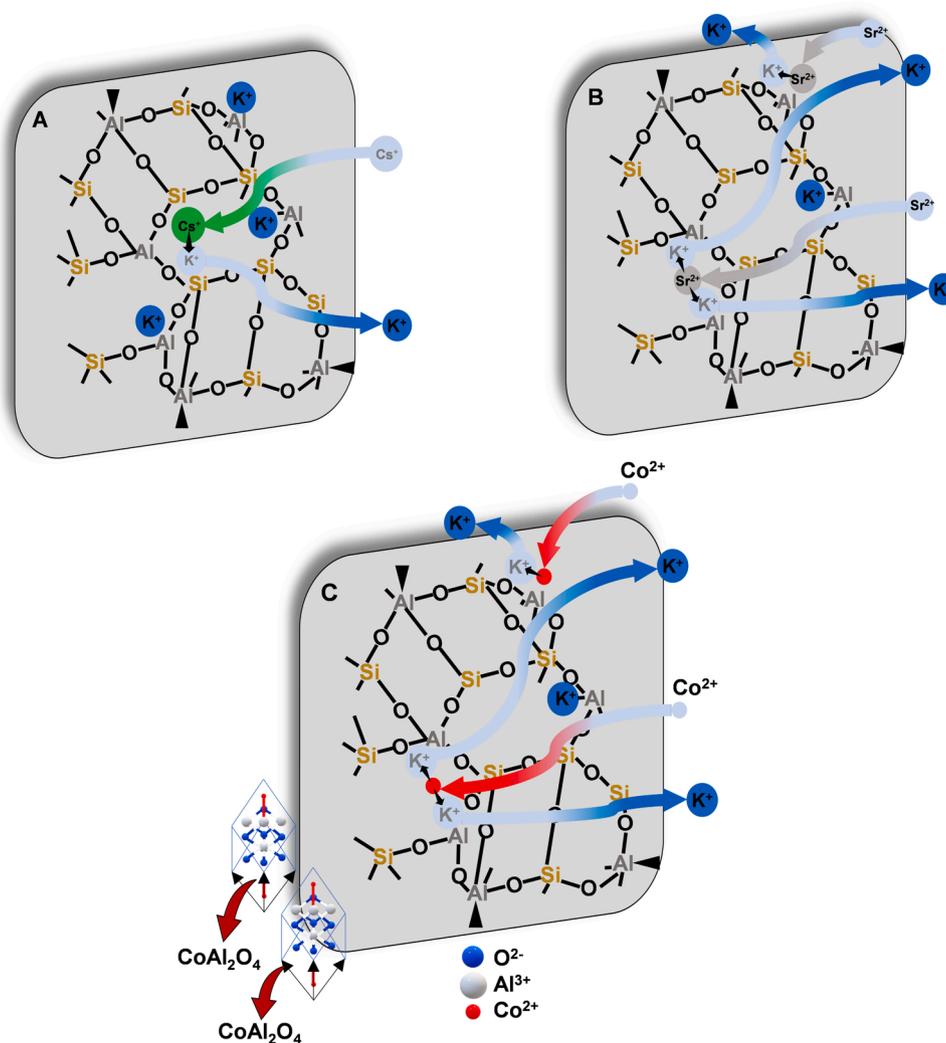
Fig. 11. Proposed binding mechanism for (A) Cs^+, (B) Sr^{2+}, and (C) Co^{2+} on geopolymer.

metakaolin-based geopolymers in terms of cation binding and K^+ leaching.

3.3. Thermodynamic modelling and verification

The ion exchange model described in Section 2.3 was used to predict the binding of Cs^+ and Sr^{2+}. In the model, the equilibrium constant is the main adjustable parameter, and can be estimated by fitting the experimental results of the leaching amount of K^+. The fitting results for Cs^+ and Sr^{2+} are shown in Fig. 10 (A) & (B). The type of metakaolin had no significant effect on leaching of K^+ (Fig. 9), and thus the fitting was conducted to the two sets of data (both MK sources) all together. A high correlation between the experimental data and modelling results was obtained for both ions in the geopolymers. The estimated equilibrium constants (log_K) for the ion exchange reaction between Cs^+ and K^+, and Sr^{2+} and K^+, were − 1.275 and − 2.025, respectively. Fig. 10 (C) & (D) shows the predicted amount of bound Cs^+ and Sr^{2+} using the estimated log_K as a function of concentration. The model prediction shows good agreement with the experimental data for Cs^+, but it underestimates the experimental data at high concentrations of Sr^{2+}. It should be noted that the predictions are based on a pure ion exchange reaction which may not consider the complete incorporation mechanism. At low concentrations of Sr^{2+}, the binding can be considered as pure ion exchange: uptake of one mole of Sr^{2+} releases two moles of K^+ (Fig. 9 (B)), and the proposed ion exchange model predicts the binding of Sr^{2+} well. This is consistent

with the results reported in previous studies (Walkley et al., 2020). At high concentrations (> 5 mmol/L), more Sr^{2+} ions are incorporated compared with the predicted result due to one-to-one ion exchange and surface complexation (as shown in Fig. 4), thus limiting the use of the proposed ion-exchange model. It should be noted that the concentration of Sr^{2+} in the nuclear waste under discussion here (polluted water) is in the order of parts per million, and the proposed pure ion-exchange model would thus be applicable. Meanwhile, the ion exchange model performed for Cs^+ and Sr^{2+} cannot be used for Co^{2+} because its uptake is not only controlled by the ion exchange mechanism (Fig. 9(C)) but also the formation of cobalt blue and surface complexation. Therefore, it is necessary to consider other mechanisms to predict their incorporation more precisely in geopolymers.

3.4. Mechanism of Cs^+, Sr^{2+} and Co^{2+} binding on metakaolin-based geopolymer

The geopolymer has a three-dimensional cross-linked structure composed of SiO_4 and AlO_4-tetrahedra which share oxygen in an alternating manner. This creates a net negative charge in the framework structure, and the alkali activator ions balance the negative charge. The constant zeta potential of the geopolymer after binding of Cs^+ ions (Fig. 4) and a one-to-one exchange between Cs^+ and K^+ ions (Fig. 9(A)) suggest that Cs^+ ions are incorporated by a pure ion-exchange mechanism, as illustrated schematically in Fig. 11(A). However, in the case of

Sr^{2+} and Co^{2+}, the ion exchange between K^+ and Sr^{2+} or Co^{2+} partially or fully compensated for the negative charge of the geopolymer, and eventually produced a positive charge (Fig. 4). This suggests that one mole of K^+ may be replaced by up to one mole of Sr^{2+} or Co^{2+}, which is significant in the Co^{2+} solution as well as at high concentrations of Sr^{2+} solution, wherein more Sr^{2+} and Co^{2+} ions are incorporated than the release of K^+ (Fig. 9). Therefore, it is believed that both one-to-two and one-to-one ion exchanges between K^+ and Sr^{2+} or Co^{2+} occur. It has been reported that the $SrCO_3$ is the main form of Sr^{2+} suppression in ion-exchanger encapsulated by geopolymer (Ke et al., 2019). It is confirmed by thermodynamic modelling as well. However, in the present study, the carbonation of Sr^{2+} in the geopolymer can be negligible and did not consider in the calculation. The binding mechanisms for Sr^{2+} and Co^{2+} are schematically shown in Fig. 11(B) and (C), respectively. The formation of cobalt blue also contributed to the removal of Co^{2+} from the aqueous solution. As shown in Fig. 9(B) and (C), the leached amount of K^+ from the geopolymer in the presence of Co^{2+} was much lower than in the presence of Sr^{2+}, even at low concentrations, thus suggesting low binding of Co^{2+} despite the formation of cobalt blue (Fig. 7).

4. Conclusions

Metakaolin-based geopolymers with the composition of $K_2O:SiO_2:H_2O$ of 1:1:13 have a high capacity to uptake cationic radionuclides such as Cs^+, Sr^{2+}, and Co^{2+}; however, the geopolymer does not have the ability to directly uptake anions of I^-, IO_3^-, SeO_3^{2-}, and SeO_4^{2-}. Specific findings from this work include:

- The geopolymers framework held a permanent negative charge in an aqueous solution.
- Ion exchange is the main mechanism for the uptake of radionuclide cations, wherein a one-to-one exchange was observed between Cs^+ and K^+ whereas both one-to-two and one-to-one exchanges were possible in the cases of Sr^{2+} and Co^{2+}. The formation of cobalt blue ($CoAl_2O_4$) also contributed to the incorporation of Co^{2+}.
- Thermodynamic modelling was conducted based on an ion exchange mechanism, which accurately predicts the binding behaviour of Cs^+ and Sr^{2+} at low concentrations. However, the model requires modification such as inclusion of precipitation and non-charge balanced ion exchange mechanism for better prediction at high concentrations of Sr^{2+} and Co^{2+}.

CRediT authorship contribution statement

Xiaobo Niu: Conceptualization, Methodology, Formal analysis, Software, Validation, Writing – original Draft, Investigation, Data Curation, Writing – review & editing. **Yogarajah Elakneswaran:** Conceptualization, Methodology, Formal analysis, Software, Supervision, Writing – review & editing. **Chaerun Raudhatul Islam:** Methodology, Investigation, Data Curation, Writing-review & editing. **John L. Provis:** Conceptualization, Methodology, Funding acquisition, Supervision, Writing – review & editing, Project administration. **Tsutomu Sato:** Conceptualization, Methodology, Funding acquisition, Supervision, Writing – review & editing, Project administration.

Declaration of Competing Interest

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

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