Article

Removal of Cesium from Radioactive Waste Liquids Using Geomaterials

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Abstract: In this study, we investigated the removal of Cs from aqueous solutions using geomaterials. Adsorption was chosen as an effective method to develop for the removal of Cs from radioactive waste liquids. Geomaterials, including fly ash and slag as raw materials, were prepared as adsorbents using an alkali activator. The materials were characterized by X-ray diffraction (XRD); scanning electron microscopy with energy dispersive spectrometer (SEM-EDS); and BET surface area, pore volume, and pore size analysis. The effects of various parameters, such as pH, contact time, and adsorbent dosage on the adsorption of the Cs were studied. The partition coefficient (PC) as well as the adsorption capacity were evaluated to assess the true performance of the adsorbent in this work. The fly ash-based geomaterials showed a maximum Cs adsorption capacity of 89.32 mg·g⁻¹ and a high PC of 31.02 mg·g⁻¹·mM⁻¹ for the Cs under our experimental conditions. From this work, this method can be regarded being practical for use as a potential adsorbent for treating Cs in wastewater. Furthermore, the immobilization of Cs in geomaterials was explored from a chemical perspective. In conclusion, fly ash-based geomaterials may be a promising option for the treatment and disposal of nuclear-contaminated waste.

Keywords: cesium (Cs); radioactive waste liquid; fly ash; geomaterials; adsorption capacity; partition coefficient

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1. Introduction

With the development of modern science and technology, nuclear energy has been widely applied in industry, national defense, agriculture, medicine, and scientific research. However, radioactive waste liquid has been produced with the rapid development of the nuclear industry. For example, due to the Fukushima Daiichi nuclear power plant accident in Japan in 2011, a significant amount of radioactive material leaked, and a substantial volume of wastewater containing radioactive cesium (Cs) was discharged. As these waste liquids are radioactive and can cause immeasurable harm to the environment and human bodies. Among them, ¹³⁷Cs is the most common radionuclide in this type of waste liquid; it produces continuous radioactivity and biological toxicity and has a half-life of about 30 years [1,2]. ¹³⁷Cs mainly releases β and γ rays, which are enriched in human muscles and expose the entire body to radiation. In addition, it may cause cell carcinogenesis, leading to long-term effects and genetic hazards, such as leukemia, infertility, and fetal malformations. The continued harm caused by the nuclear leakage accident at the Fukushima Daiichi Nuclear Power Plant once again sounds the alarm for humankind [3–6]. Due to this disaster, the removal of radioactive cesium as well as strontium in water has gained considerable attention from many scholars around the world.

The current removal methods for radioactive cesium mainly include chemical precipitation [7–10], solvent extraction [11–14], membrane separation [15–18], biological treatment [19,20], and adsorption [21–24]. The adsorption method is widely used in the removal of radionuclides in water due to its high efficiency, simplicity, high selectivity, and strong adaptability. In recent years, the most versatile inorganic materials that have been used to remove radioactive cesium in water mainly include geopolymers, nano-carbon materials, and metal oxides, among others [25–27].

Geomaterial [28] is a type of inorganic cementitious polymer material that has been developed in recent years. It uses calcined clay (metakaolin), volcanic pumice, fly ash, mineral waste slag, and other silico-alumina materials as raw materials. Under the action of the activator, a polymerization reaction occurs to form a three-dimensional, network-like, high-strength dense material that is mainly composed of silicon–oxygen tetrahedrons and aluminum–oxygen tetrahedrons and that has amorphous and quasi-crystalline characteristics.

With regard to the current problem of the solidification of heavy metal and radioactive waste, this study proposes a practical solution. For our experiments, we used synthetic fly ash-based geomaterials at room temperature, which can overcome some of the consequences of solidified heavy metal and nuclear waste, both locally and abroad. It has the advantages of a low solidification treatment cost, a simple and easy-to-control process, and it can reduce or avoid secondary pollution. This study provides a theoretical basis for the optimization and preparation of adsorption materials with high-efficiency adsorption performance and lays a foundation for the solidification of heavy metal and nuclear waste and their safe adsorption and disposal. It is of great significance to the healthy and sustainable development of the modern economy.

2. Materials and Methods

The main chemical components of ordinary Portland cement, fly ash, and slag are CaO, SiO₂, Al₂O₃, Fe₂O₃, MgO, and TiO₂. These chemical reagents were purchased from Kanto Chemical Co., Ltd. (Tokyo, Japan). The reagents NaOH, sodium silicate, and CsCl were of analytical grade and were also purchased from Kanto Chemical Co., Ltd. (Tokyo, Japan). In addition, a BT100 Water Bath Incubator (Yamato Kagaku Co., Ltd., Tokyo, Japan), a DP33 Vacuum Drying Oven (Yamato Kagaku Co., Ltd., Tokyo, Japan), a pH meter (HORIBA F-72, Tokyo, Japan), an X-ray diffractometer (XRD, D2 Phaser, Bruker, Yokohama, Japan), a scanning electron microscope and an energy dispersive spectrometer (SEM-EDS, JEOL, Akishima City, Tokyo, Japan: JCM-6000 with JED-2300), and a specific surface area and pore size analyzer (N₂-BET; TriStar 3020, Micromeritics, Norcross, GA, USA) were employed in this work.

2.1. Synthesis of the Adsorbent

CaO, SiO₂, Al₂O₃, Fe₂O₃, MgO, and TiO₂ were mixed in a certain weight ratio, listed in Table 1, to prepare ordinary Portland cement, fly ash, and slag. The fly ash and slag were used as geomaterials, and the Portland cement was used as a reference material.

Table 1. Chemical compositions of the raw materials.

Chemical Compositions	Weight of Mixture (g)		
	Portland Cement	Fly Ash	Slag
CaO	15.6	2.65	23.9
SiO ₂	5.25	25.8	16.2
Al ₂ O ₃	1.48	11.0	5.75
Fe ₂ O ₃	0.800	5.40	0.300
MgO	0.700	1.00	1.50
TiO ₂	-	0.800	0.250

The Portland cement paste was produced with a mixture of water and cement at a ratio of 0.5. The fly ash-based geomaterial was produced from a mixture of liquid (alkali

activator) and solid (fly ash) at a ratio of 0.5. A mixture of a 9M NaOH solution and a sodium silicate solution at a weight ratio of 1:1 was used as an alkali activator. The slag-based geomaterials were produced by replacing 50% of the fly ash with slag by weight. The slag-based geomaterials were produced with mixtures of liquid (alkali activator) and solid (fly ash and slag) at a ratio of 0.5, identical to those of the other matrices. The alkali activator used for the slag-based geomaterials matrix was composed of a 4 M NaOH solution and a sodium silicate solution at a weight ratio of 2:1. The mixed samples were stirred for 3 to 5 min. Then, they were transferred to a 200 mL Erlenmeyer flask, shaken in a water bath with a constant temperature (25 °C) for 24 h, and cured for 7 d. After drying at a constant temperature of 105 °C for 24 h, they were put into a cylindrical vial with a diameter of 25 mm and a height of 50 mm.

In order to study the interaction between the adhesive matrix and cesium, a test sample containing stable cesium (^{133}Cs) was prepared. The analytical reagent CsCl was used to simulate radioisotopes (^{137}Cs). Then, $12.67 \text{ g}\cdot\text{L}^{-1}$ of CsCl was added to the adhesive, and up to $10 \text{ g}\cdot\text{L}^{-1}$ of Cs^+ were added, depending on the volume of the sample. Before mixing the samples, the CsCl was dissolved in the alkali activator.

2.2. Characterization of the Adsorbent

In this study, the material characterization methods were X-ray diffraction (XRD), scanning electron microscopy and energy dispersive spectrometer (SEM-EDS), and Brunauer–Emmet–Teller (BET) surface area, pore volume, and pore size analysis.

In order to identify changes in the crystalline phase caused by incorporating cesium into the solidified matrix, XRD analysis was performed on the sample, and the XRD data were collected with a scan range of 5° to 60° . The obtained characteristic diffraction peaks determined the type of crystal structure and material. The surface morphology and Cs distribution of the materials were observed by SEM-EDS. SEM was also used to determine the surface morphology of the materials. The BET surface area and pore size distribution were measured by N_2 gas adsorption on the instrument. The sample was degassed at 150°C for 3 h and was then subjected to a N_2 adsorption/desorption test.

2.3. Adsorption Experiments

In order to study the effects of pH, adsorbent usage, contact time, and initial concentration on the adsorption of Cs, the following adsorption experiments were conducted. After the geomaterials were passed through a 720 mesh sieve, they were transferred to a 200 mL Erlenmeyer flask with 100 mL of Cs solution with a known concentration, and were then placed in a constant temperature shaker (TAITEC Plus Shaker EP^{-1} with Thermo Minder SX-10R, Saitama, Japan) set at a prescribed temperature. The temperature of the adsorption experiment was 25°C , the pH values were 3, 4, 5, 6, 7, 8, and 9; the amounts of adsorbent used were 0.05 g, 0.1 g, 0.2 g, 0.4 g, 0.6 g, and 0.8 g; the contact times were 1 h, 3 h, 8 h, 24 h, and 72 h; and the initial concentrations were $5 \text{ mg}\cdot\text{L}^{-1}$, $10 \text{ mg}\cdot\text{L}^{-1}$, $20 \text{ mg}\cdot\text{L}^{-1}$, $30 \text{ mg}\cdot\text{L}^{-1}$, and $40 \text{ mg}\cdot\text{L}^{-1}$. The pH value was adjusted by using aqueous HCl and aqueous NaOH.

Following each adsorption experiment, the suspension containing geomaterials and the above standard solution were filtered through a $0.45 \mu\text{m}$ membrane filter (Mixed Cellulose Ester, 47 mm, Advantec, Tokyo, Japan) to remove the Cs^+ that had been adsorbed into the geomaterials, and the concentration of the Cs in the filtrate was determined with the ICP-MS (Thermo Scientific Center: X-series II, Waltham, MA, USA). The adsorption capacity of the geomaterials for the Cs ions was calculated by Equation (1).

$$q_e = \frac{(C_i - C_e)}{m} \cdot V, \quad (1)$$

where q_e represents the adsorption capacity at equilibrium ($\text{mg}\cdot\text{g}^{-1}$); C_i and C_e are the initial and equilibrium Cs concentrations ($\text{mg}\cdot\text{L}^{-1}$) in the solution, respectively; V is the volume of the solution (L); and m is the mass of adsorbent (g) [29–31].

2.4. Adsorption Isotherm

In the adsorption process, study of the equilibrium isotherm is necessary and crucial to predict the adsorption behavior of the pollutants towards the adsorbent surface. In this study, two common adsorption models, the Langmuir and Freundlich isotherm models, were used to evaluate adsorption data.

The Langmuir isotherm model assumes that the adsorption process occurs in a single layer of gas–solid two-phase adsorption and is given by Equation (2):

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{K_L q_{\max}} \quad (2)$$

where C_e is the concentration of Cs in a batch system at equilibrium ($\text{mg}\cdot\text{L}^{-1}$), q_e is the amount of f Cs adsorption at equilibrium ($\text{mg}\cdot\text{g}^{-1}$), $q_{\max}$ is the maximum adsorption capacity of the adsorbent ($\text{mg}\cdot\text{g}^{-1}$), and K_L is the equilibrium adsorption constant ($\text{L}\cdot\text{mg}^{-1}$). A plot of C_e/q_e versus C_e gives a straight line with a slope of $1/q_{\max}$ and an intercept of $1/(K_L q_{\max})$. K_L can be applied to the adsorption free energy ΔG_{ads} ($\text{J}\cdot\text{mol}^{-1}$) by Equation (3):

$$n\Delta G_{\text{ads}} = -RT \ln K_L \quad (3)$$

where R is the gas constant ($8.314 \text{ J}\cdot\text{K}^{-1}\text{mol}^{-1}$), T is the absolute temperature at equilibrium (K), and K_L is the equilibrium constant at temperature T .

The equilibrium constant [32,33] K_L can be calculated according to Equation (4):

$$K_L = q_e / C_e \quad (4)$$

where C_e and q_e are the same as in Equation (2).

The Langmuir constant (K_L) can be used to determine the suitability of the adsorbent for the adsorbate by using the dimensionless parameter of the Hall separation coefficient (R_L), which is given by Equation (5):

$$R_L = \left(\frac{1}{1 + K_L C_0} \right) \quad (5)$$

where C_0 ($\text{mg}\cdot\text{L}^{-1}$) is the initial concentration [34,35].

The Freundlich isotherm model is a multi-layer adsorption process that does not consider adsorption saturation, which occurs on a multi-layer heterogeneous surface. The isotherm of the linear Freundlich model is expressed by Equation (6):

$$\ln q_e = \ln K_F + (1/n) \ln C_e \quad (6)$$

where K_F is the adsorption capacity ($(\text{mg}\cdot\text{g}^{-1})\cdot(\text{dm}^{-3}\cdot\text{mg}^{-1})^{1/n}$), and $1/n$ is the adsorption strength. The logarithmic scale graph of q_e versus C_e can be drawn to determine the $1/n$ and K_F values, and the value of $1/n$ can be used to judge the difficulty of the adsorption process [36].

2.5. Kinetic Studies

The rate equation for a chemical reaction is an equation that links the reaction rate with concentrations or pressures of reactants and constant parameters (normally rate coefficients and partial reaction orders). For many reactions, the rate is given by a power law, such as Equation (7):

$$r = k[A]^x[B]^y \quad (7)$$

where $[A]$ and $[B]$ express the concentrations of the species A and B, respectively (usually in moles per liter (molarity, M)). The exponents x and y are the partial reaction orders and must be determined experimentally; they are often not equal to the stoichiometric coefficients [32–35]. The constant k is the rate coefficient or rate constant of the reaction.

The value of this coefficient k may depend on conditions such as the temperature, ionic strength, and surface area of an adsorbent or light irradiation.

A kinetic model has been proposed to determine the mechanism of the adsorption process, which provides useful data to improve the adsorption efficiency and the feasibility of scaling up the process [37,38]. In the present investigation, the mechanism of the adsorption process was studied by fitting pseudo-first-order and pseudo-second-order reactions to the experimental data.

The pseudo-first-order model is given by Equation (8):

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \quad (8)$$

where q_e and q_t are the adsorption capacity ($\text{mg} \cdot \text{g}^{-1}$) of the adsorbent to adsorb Cs^+ at the equilibrium time and time t , respectively, and k_1 is the rate constant (h^{-1}) of the pseudo-first-order adsorption.

The pseudo-second-order rate Equation (9) is expressed as follows:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e} \quad (9)$$

where k is the rate constant of pseudo-secondary adsorption ($\text{g} \cdot \text{mg}^{-1} \cdot \text{h}^{-1}$), and where q_e and q_t are the adsorption capacity of adsorbent for Cs^+ at the equilibrium time and time t , respectively ($\text{mg} \cdot \text{g}^{-1}$).

3. Results and Discussion

3.1. Adsorption Experiment

3.1.1. Effect of pH on the Adsorption of Cs

The pH value of the aqueous solution will affect the surface charge of the adsorbent, the ionization degree and morphology of the metal ions, and the surface metal-binding sites. Under the conditions of the pH values of 3, 4, 5, 6, 7, 8, and 9, all other parameters were kept unchanged (adsorbent usage: 0.1 g; contact time: 24 h; initial concentration: $0.79 \text{ mg} \cdot \text{L}^{-1}$; and temperature: 298 K). The effect of pH on the adsorption of Cs^+ was studied. The results are shown in Figure 1. The maximum adsorption capacity of Cs^+ was obtained at pH 8, which may be related to the alkaline nature of the geomaterials. Therefore, a pH of 8 was selected for further study.

Figure 1. Effect of pH on the adsorption of Cs by fly ash-based geomaterials and slag-based geomaterials.

3.1.2. Effect of the Adsorbent Dosage on the Adsorption of Cs

The amount of adsorbent used is an important factor affecting the adsorption capacity. In order to determine the effect of the amount of adsorbent on the removal of Cs^+ , the adsorbent dosage was varied (0.05 g, 0.1 g, 0.2 g, 0.4 g, 0.6 g, and 0.8 g) under other fixed conditions (temperature: 298 K; contact time: 24 h; and initial concentration: $0.79 \text{ mg}\cdot\text{L}^{-1}$). The results are shown in Figure 2. It can be seen from the figure that as the adsorbent dosage increased, the removal rate increased significantly. For the adsorbent dosage of 0.6 g, it can be observed that more than 80% of Cs^+ was removed; when the adsorbent dosage was greater than 0.6 g, the adsorption capacity did not increase significantly. Therefore, 0.6 g was considered to be the optimal dosage for Cs adsorption for further study.

Figure 2. Effect of sorbent dosage on the adsorption of Cs by fly ash-based geomaterials and slag-based geomaterials.

3.1.3. Effect of Contact Time on the Adsorption of Cs

The influence of contact time on Cs adsorption by the geomaterials was explored. In this study, the adsorption of $0.79 \text{ mg}\cdot\text{L}^{-1}$ of Cs^+ was conducted using 0.6 g of adsorbent under the conditions of a temperature of 25°C and a pH of 8. The Cs^+ adsorption amount by the geomaterials was measured when the contact time was 1 h, 3 h, 8 h, 24 h, and 72 h, and the results are shown in Figure 3. This study also verified the kinetics of the adsorption process, which are presented in Section 3.3. It was observed that the Cs adsorption capacity of the geomaterials increased sharply in the first 3 h, and until the contact time of 24 h, the adsorption capacity of Cs gradually increased; there was no significant change thereafter. Therefore, 24 h was chosen as the best contact time for further study.

3.2. Characterization of Geomaterials

The influence of the doped Cs on the crystal structure of the adhesive was investigated by XRD, and the results are shown in Figure 4. In the Portland cement binder, the addition of Cs did not cause the formation of a crystalline phase but led to the formation of Friedel's salt, which was due to the sulfate ion in monosulfate (AFm) or ettringite (AFt) being replaced by a chloride ion. This indicates that the chloride ions from cesium chloride resulted in the formation of Friedel's salt [37,38]. In the fly ash-based geomaterials, the crystalline phases were mullite, quartz, coesite, hematite, and magnetite, that is, the non-reactive crystalline phase present in the original fly ash. The crystalline phase in the slag-based geomaterials was similar to the fly ash-based geomaterials, and the peak corresponding to C-S-H increased with increasing the slag content. No cesium-containing

crystalline phase was observed, which is similar to the results of the Portland cement and the fly ash-based geomaterials.

Figure 3. Adsorption capacity of fly ash-based geomaterials and slag-based geomaterials for Cs adsorption.

Figure 4. XRD of some geomaterials before and after the incorporation of Cs. P: portlandite, H: hematite, Ma: magnetite, C: C–S–H, M: mullite, Q: quartz, Co: coesite, T: tricalcium silicate, D: dicalcium silicate.

The SEM and element mapping of the geomaterial matrices are shown in Figure 5. From the SEM images, we can see the flocculated substance and crystal, among which the flocculated substance is amorphous silicon aluminate. The SEM images of the Portland cement and slag-based geomaterials show that the whole material structure is relatively compact, and the pores are small. The morphological characteristics of fly ash-based geomaterials is similar to that of Zhao [39], who used alkali slag-modified alkali to stimulate fly ash-based geopolymer gels, but the pores of the fly ash-based geomaterials are larger. The white sediment in the geomaterials may be formed by Cs, which is evenly distributed, and the location is not concentrated. It is important to note a negative correlation between

Cs and Na can be found in the element mapping image. This correlation could be the evidence of the typical cation exchange reactions that occur in geotechnical materials, in which sodium zeolite or its precursor exchanges its charge-balanced cations. Specifically, molecular sieves or their precursors serve as adsorption sites where sodium is replaced by cesium [40,41].

(A)

Figure 5. Cont.

(B)

Figure 5. Cont.

Figure 5. SEM and element mapping images of the geomaterial matrices. (A) Portland cement, (B) fly ash, (C) slag.

The specific surface areas of ordinary Portland cement, fly ash-based geomaterials, and slag-based geomaterials were measured by N_2 adsorption. The pore characteristics of the powder binder determined by the BET method are summarized in Table 2. These results indicate that the fly ash-based geomaterials had the highest surface area and micropore volume and that the pore characteristics of the fly ash-based geomaterials were the most suitable for the adsorption of Cs, which is consistent with the SEM results. This also indicates that fly ash-based geomaterials may be the most effective in terms of chemical barriers to prevent the release of cesium.

Table 2. The BET surface area, pore size, and pore volume of Portland cement, fly ash, and slag.

Sample	BET Surface Area [m ² ·g ^{−1}]	Pore Volume [cm ³ ·g ^{−1}]	Pore Size [nm]
Portland Cement	0.9582	0.002652	11.07
Slag	1.388	0.004432	12.77
Fly Ash	1.869	0.006359	13.61

3.3. Adsorption Kinetics Study

The adsorption kinetics study was conducted to explore the relationship between the adsorption amount q_t and t . As seen in Figure 3, the adsorption capacity of the fly ash-based and slag-based geomaterials on Cs⁺ increased significantly within 24 h. In order to understand the adsorption kinetics in more detail, the mechanism of the adsorption process was studied by fitting the pseudo-first-order reactions and pseudo-secondary reactions to the experimental data of this study. In order to investigate the consistency between the model and the experimental results under the optimized experimental conditions, the pseudo-first-order and pseudo-secondary results were used to apply the linear graphs of $\ln(q_e - q_t) - t$ and $t/q_t - t$ to the Cs adsorption kinetic model, as shown in Figures 6 and 7, respectively. Table 3 shows the linear constants (R^2) and the other parameters of the two kinetic models of Cs⁺ adsorption to geomaterials calculated from Figures 6 and 7. For the cesium adsorption kinetics of the slag-based geomaterials, the pseudo-first-order model has a higher R^2 value than that of the pseudo-second-order model, indicating that the adsorption process was mainly physical adsorption. On the other hand, the Cs adsorption kinetics of the fly ash-based geomaterials is in good agreement with the pseudo-secondary model, which indicates that chemical adsorption was more dominant. This can be explained by the fact that the fixation mechanism of Cs in alkali-activated fly ash is controlled by the cation exchange mechanism [42].

Figure 6. Pseudo-first-order linear kinetic model of Cs adsorption on the fly ash-based geomaterials and slag-based geomaterials.

Figure 7. Pseudo-second-order linear kinetic model of Cs adsorption on the fly ash-based geomaterials and slag-based geomaterials.

Table 3. Parameters for two kinetic models of Cs adsorption by fly ash-based geomaterials and slag-based geomaterials.

Sample	q_{exp} (mg/g)	Pseudo-First-Order			Pseudo-Second-Order		
		q_e (mg·g ⁻¹)	k_1 (h ⁻¹)	R^2	q_e (mg·g ⁻¹)	k_2 (g·mg ⁻¹ ·h ⁻¹)	R^2
Fly ash	83.68	53.20	0.03620	0.6936	85.82	12.83	0.9955
Slag	60.93	60.67	0.1812	0.9994	31.71	12.40	0.9989

3.4. Adsorption Isotherm Study

The adsorption isotherm is usually used to reflect the performance of the adsorbent in the adsorption process. In order to quantify the adsorption capacity of the adsorbent to remove Cs, Langmuir and Freundlich's isotherms were used in this study. Under optimal adsorption conditions (pH of 8, contact time of 24 h, adsorbent dosage of 0.6 g), the adsorption isotherm model of Cs⁺ on the geopolymer was established at the initial concentrations of 5 ppm, 10 ppm, 20 ppm, 30 ppm, and 40 ppm. The results of the adsorption data investigated by the Langmuir and Freundlich models are shown in Figures 8 and 9, respectively. Other parameters, including the correlation coefficient (R^2), are given in Table 4. The correlation coefficient shows that the Langmuir isotherm can describe the adsorption of Cs better than Freundlich's isotherm model can. This result shows that the adsorption of Cs⁺ by geomaterials mainly occurs through a single-layer reaction, and the maximum adsorption capacity is estimated to be 89.32 mg·g⁻¹. The attached isotherm parameters show that the fly ash-based geomaterials are more effective for adsorbing Cs ions.

Table 4. Coefficient of Langmuir and Freundlich isotherms for Cs.

Sample	Langmuir Isotherm			Freundlich Isotherm		
	q_{max} (mg·g ⁻¹)	K_L (L·mg ⁻¹)	R^2	K_F ((mg·g ⁻¹)· (dm ⁻³ ·mg ⁻¹) ^{1/n})	1/n	R^2
Fly ash	89.32	0.1665	0.9948	10.75	0.01620	0.1309
Slag	44.52	0.02126	0.9954	20.55	0.04660	0.3698

Figure 8. The Cs adsorption of the Langmuir isotherm on the fly ash-based geomaterials and slag-based geomaterials.

Figure 9. The Cs adsorption of the Freundlich isotherm on the fly ash-based geomaterials and slag-based geomaterials.

3.5. Adsorption Mechanism

The adsorption of cesium on fly ash-based geomaterials and geomaterials doped with slag was studied. The influence of the pH of the solution, the adsorbent dosage, and the contact time on the adsorption efficiency were discussed. The following matters can be considered:

- (1) The adsorption experiment data of Cs on fly ash-based geomaterials and slag-based geomaterials conform to the Langmuir isotherm adsorption equation. The isothermal fitting of the Langmuir model shows that the surface is heterogeneous, which indicates that the adsorption of Cs on the surface of the adsorbent mainly occurred as single-layer adsorption.
- (2) The best fit was obtained with the pseudo-second-order kinetic model while investigating the adsorption kinetics of Cs adsorption on the fly ash-based geomaterials, indicating that the adsorption process was mainly chemical adsorption. The R^2 was greater than 0.996. On the other hand, Cs adsorption on the slag-based geomaterials was suitably described by the pseudo-first-order model as well as by the pseudo-

second-order model (the R^2 values were both about 0.999), indicating that physical as well as chemical adsorption were dominant in the adsorption process.

The results show that the fly ash-based geomaterials can remove Cs^+ more effectively. The adsorption kinetics of the geomaterials with higher adsorption capacities are compatible with the pseudo-two-stage kinetic model, which indicates that it is controlled by complex multi-step adsorption. The negative correlation between cesium and sodium is evidence of a typical cation exchange reaction that occurs in fly ash-based geomaterials, in which sodium zeolite or its precursor exchanges its charge-balancing cations. Specifically, zeolite or its precursor is provided as an adsorption site, where sodium is replaced by cesium [40,41]. Calcium silicate hydrate geomaterials may interact with the adsorbate by a weak interaction through van der Waals forces (i.e., Physisorption). On the other hand, the (sodium)-aluminosilicate-hydrate geomaterials may share or exchange electrons (cations) between the adsorbent and the adsorbate (i.e., Chemisorption). These results provide new insights, demonstrating that the properties of aluminosilicate geomaterials with a large microporous surface area promote more effective cesium fixation compared to calcium silicate hydrate.

3.6. Comparison with Other Adsorbents

For many adsorption studies, the performance of the adsorbent is generally estimated and expressed by the maximum (or equilibrium) adsorption capacity. However, the maximum adsorption capacity is sensitively affected by the initial loading concentration of target pollutant (or more specifically what is left after sorption reaction).

(If the sorbent is exposed to a higher concentration of targets, it is apt to exhibit a higher adsorption capacity. On the other hand, if the sorbent is exposed to lower levels of target species, it will show lower capacities.)

Then, in addition to the maximum adsorption capacity, it is effective to estimate using the concept of partition coefficient (PC) as explained below as the following our references.

$$\text{PC} = \text{Adsorption capacity} / \text{Final concentration}$$

$$(\text{or} = \text{Adsorption capacity} / (\text{Initial concentration} \times \text{removal ratio})).$$

From Table 5, it can be seen that the maximal adsorption capacity of the fly ash-based geomaterial in this study is not notably high ($89.32 \text{ mg} \cdot \text{g}^{-1}$) compared to the other adsorbents. However, it is noteworthy that the PC value of this adsorbent is fairly high ($31.02 \text{ mg} \cdot \text{g}^{-1} \cdot \text{mM}^{-1}$). It can then be regarded as a potential adsorbent for treating Cs in wastewater for practical use, especially when also considering that the synthesis method of the adsorbent is simple.

Table 5. The comparison of adsorption properties of several adsorbents.

Adsorbents	Final Concentration ($\text{mg} \cdot \text{L}^{-1}$)	Adsorption Capacity ($\text{mg} \cdot \text{g}^{-1}$)	Partition Coefficient ($\text{mg} \cdot \text{g}^{-1} \cdot \text{mM}^{-1}$)	Reference
nFe/Cu-Z	26.28	77.51	2.949	[43]
Natural clinoptilolite from Serbia	76.00	49.26	0.6482	[44]
Nanocrystalline mordenite (pulverized)	4.000	37.30	9.325	[45]
MWCNT reinforced zeolite-A beads	30.00	113.0	3.767	[46]
Carbon-zeolite	156.0	120.9	0.7750	[47]
Natural mordenite	9.574	254.8	26.61	[48]
Synthetic mordenite	9.508	220.4	23.18	[48]
Phosphoric acid activated montmorillonite	13.30	208	15.64	[49]
Ethyl-VER	2.161	43.96	20.34	[50]
Bentonite	8.700	177.4	20.39	[51]
Clinoptilolite	12.50	12.50	1.000	[52]
Fly ash-based geomaterials	2.879	89.32	31.02	This study

In recent years, a lot of research has focused on the solidification of radioactive waste-based on geomaterials, but the current understanding of the fixing mechanism

is not necessarily sufficient. This study mentioned the fixation mechanism of Cs in the solidification of geomaterials, especially in terms of chemistry.

4. Conclusions

Based on the static adsorption test, the adsorption performance of Cs on geomaterials was studied, and the influence of various factors on the adsorption performance was discussed. Constructing the foundation for the further solidification of waste containing radioactive elements was examined in this work. The geomaterials were synthesized from fly ash and slag, and the synthesized geomaterials were characterized by XRD, SEM, and N₂-BET. The adsorption efficiency of the fly ash-based geomaterials and the geomaterials doped with slag as adsorbents for removing Cs was evaluated. The effects of the pH, adsorbent dosage, and contact time on Cs removal were investigated. Furthermore, the Langmuir and Freundlich models were used to describe the adsorption equilibrium mathematically. From this work, the fly ash-based geomaterials showed a maximum Cs adsorption capacity of 89.32 mg·g⁻¹ and a high PC of 31.02 mg·g⁻¹·mM⁻¹ for Cs. Additionally, the applicability of the kinetic model to the adsorption process was also discussed.

Through this work, it was proved to a certain extent that the fly ash-based geomaterials adsorb Cs more efficiently and that they have considerable potential to be applied as adsorbents for removing Cs. Furthermore, the immobilization of Cs in geomaterials was explored from a chemical perspective. From the perspective of environmental protection, fly ash can be used to treat nuclear waste containing radioactive nuclear waste liquid. In conclusion, fly ash based-geomaterials may be a promising option for the treatment and disposal of nuclear-contaminated waste.

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