

Kinetics of Cs(I), Sr(II), and Re(VII) Sorption on Metakaolin-based Alkali-activated Material and Gyeongju LILW Repository Concrete

Hyeonjin Eun, Sajid Iqbal, Jisoo Jung, Jong-Il Yun*

Department of Nuclear and Quantum Engineering, Korea Advanced Institute of Science and Technology, 291
Daehak-ro, Yuseong-gu, Daejeon, 34141

*Corresponding author: jiyun@kaist.ac.kr

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1. Introduction

Alkali-activated materials (AAMs), often broadly referred to as geopolymers, have attracted considerable attention as low-CO₂ cementitious alternatives to conventional Portland cement concrete [1–3]. AAMs have also been extensively studied as potential alternatives to cement-based waste forms for radioactive waste immobilization [4–6]. Sorption behavior provides a useful basis for evaluating the extent of radionuclide immobilization. However, to the best of the authors' knowledge, direct comparisons of radionuclide sorption by concrete and AAMs under identical experimental conditions remain scarce. In this study, the sorption characteristics of Cs and Sr, which are radionuclides of concern, and Re(VII), considered a chemical analogue of Tc(VII), were compared between metakaolin-based AAM (MK-AAM) and Gyeongju LILW Repository concrete, with particular emphasis on sorption kinetics.

2. Methods and Results

2.1 Sorbent Materials Preparation

The concrete used in this study was an OPC concrete blended with 20% fly ash. It was produced during the Phase 2 construction of the Gyeongju LILW repository and provided by the Korea Radioactive Waste Agency (KORAD).

The pristine MK-AAM, which contained no radionuclides, was prepared following the same procedure described in our previous study [6], where detailed mixture proportions are provided. Metakaolin was mixed with a NaOH–sodium silicate activator, cast into molds, and cured at ambient temperature for 24 h, followed by curing at 60 °C for 6 days.

Following the procedure described in our previous study [7], both the concrete and MK-AAM were crushed, sieved to a particle size of 0.6–1.0 mm, washed with deionized water for 3 weeks, and dried overnight at 60 °C.

2.2 Batch Sorption Experiment

Sorption samples were prepared by adding 2.0 g of crushed concrete or MK-AAM to 50 mL polypropylene

tubes, followed by 40 mL of a pH 10 (0.1 mM NaOH) background solution containing 0.01 M NaCl, corresponding to a solid-to-liquid ratio of 50 g/L. After 24 h of pre-equilibration, 0.4 mL aliquots of 1 mM CsCl, SrCl₂, and NaReO₄ stock solutions were added to achieve a nominal final concentration of ~10 μM for each element. The samples were mixed on a horizontal roller mixer at 10 rpm, and 0.5 mL aliquots of the solution were collected after 30 min, 1 h, 3 h, 12 h, 1 day, 4 days, 7 days, and 13 days. The concentrations of Cs, Sr, and Re in the collected solutions were determined by inductively coupled plasma–mass spectrometry (ICP-MS). After 13 days of sorption, the measured pH values were 9.02±0.02 for the MK-AAM samples and 11.19±0.04 for the concrete samples.

2.3 Kinetic Models

The amount sorbed per unit mass of sorbent at time t was calculated using the following equation (Eq.(1)):

$$q(t) = \{C_0 - C(t)\} \times V / m \quad (1)$$

where C_0 is initial concentration, $C(t)$ is the concentration in the solution at time t , V is the liquid volume, and m is the sorbent mass.

Sorption kinetics were modeled using the pseudo-first-order (Eq.(2)) and pseudo-second-order (Eq.(3)) kinetic models [8]:

$$q(t) = q_e \{1 - \exp(-k_1 t)\} \quad (2)$$

$$q(t) = q_e^2 k_2 t / (1 + q_e k_2 t) \quad (3)$$

where q_e is the amount sorbed per unit mass of sorbent at equilibrium, k_1 and k_2 are the rate constants for the pseudo-first-order and pseudo-second-order models.

2.4 Aqueous speciation calculation

The distribution of aqueous species in the batch systems was calculated using the ThermoChimie database (Version 13a) and PHREEQC (Version 3). Because Re is not included in ThermoChimie Version 13a, thermodynamic data for Re were supplemented from the literature [9]. The calculated aqueous species distributions in the absence of precipitation are shown in Fig. 1.

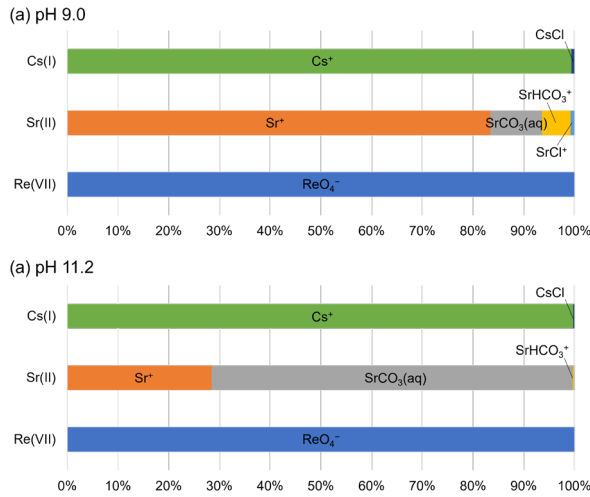


Fig. 1. Calculated speciation of Cs(I), Sr(II), and Re(VII) at (a) pH 9.0 (MK-AAM) and (b) pH 11.2 (Concrete).

2.5. Sorption Results

Fig. 2 shows the changes in the amounts of Cs(I), Sr(II), and Re(VII) sorbed onto MK-AAM and concrete as a function of time. Both sorbents exhibited strong sorption of Cs(I) and Sr(II), whereas only very weak sorption of Re(VII) was observed. As shown in Fig. 1, perhenate, an anionic species ReO_4^- , exhibits negligible sorption because it is electrostatically unfavorable for it to interact with predominantly negatively charged aluminosilicate surfaces.

Although the sorbed amounts of Cs(I) and Sr(II) appeared to be higher for MK-AAM than for concrete, the Ar-BET specific surface area of MK-AAM ($41 \pm 2 \text{ m}^2/\text{g}$) was much larger than that of concrete ($2.1 \pm 0.1 \text{ m}^2/\text{g}$). When normalized by specific surface area, therefore, concrete exhibited a higher sorbed amount per unit surface area. The aggregates in the concrete contain mica minerals. Previous studies have reported that the presence of mica minerals in concrete aggregates can result in strong sorption of radionuclides such as Cs(I) [8,10].

Based solely on the time required to reach equilibrium, sorption onto MK-AAM was much faster than that onto concrete. Quantitative kinetic parameters could not be obtained for MK-AAM because sorption equilibrium had already been reached by the first sampling time of 30 min, leaving insufficient data points in the kinetic region for model fitting. In contrast, concrete required more than one day to reach equilibrium, allowing its sorption kinetics to be fitted using the pseudo-first-order and pseudo-second-order models.

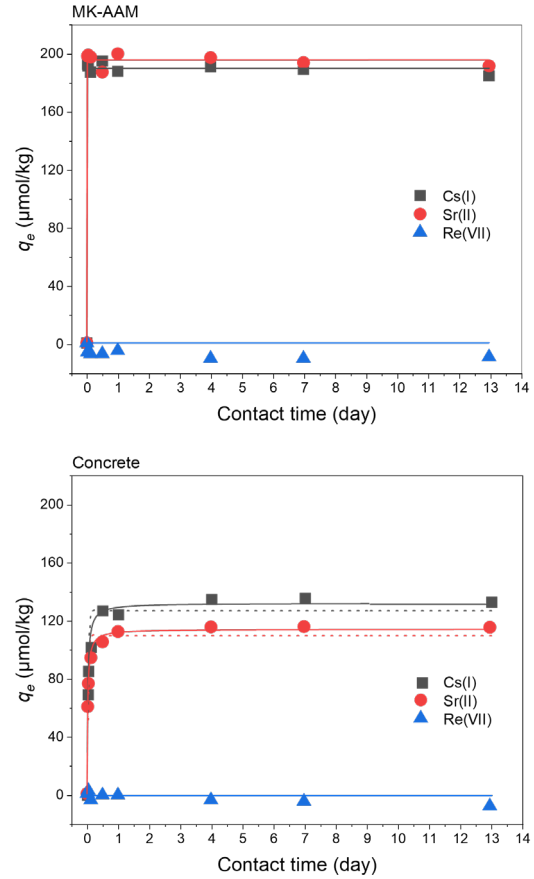


Fig. 2. Amount sorbed (q_e) as a function of contact time for metakaolin based alkali-activated material (MK-AAM) and Gyeongju LILW concrete. Solid lines represent fits to the pseudo-second-order model, and dashed lines represent fits to the pseudo-first-order model.

As reported in our previous studies, radionuclides such as Cs(I) are known to require considerable time to diffuse into the interlayer regions of mica minerals [7,8]. The sorption kinetics of Cs(I) were far slower in biotite gneiss than in granite, in contrast to Ni(II), for which interlayer diffusion is less significant [7]. Our group also reported that, in the same crushed concrete used in the present study, Cs(I) exhibited a sorption distribution coefficient comparable to that of U(VI), which is likewise less affected by interlayer diffusion, but eluted more rapidly in column transport experiments because of its slower sorption kinetics [8]. Consequently, their sorption kinetics are slower than those in pure AAMs without such minerals because interlayer diffusion in mica acts as the rate-limiting step.

3. Conclusions

The extent and kinetics of Cs(I), Sr(II), and Re(VII) sorption onto MK-AAM and concrete were evaluated. Owing to its larger specific surface area, MK-AAM exhibited higher sorption amounts per unit mass than concrete, whereas its sorption site density was lower

than that of concrete containing strongly sorbing mineral in aggregates. Sorption onto concrete was substantially slower than onto MK-AAM, which was attributed to the relatively slow interlayer diffusion of radionuclides into mica-group minerals. Both materials exhibited negligible sorption of Re(VII), a chemical analogue of Tc(VII), indicating that additional retardation mechanisms may be required for effective immobilization of anionic radionuclides.

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