Task-Specific Tailored Cationic Polymeric Network with High Base-Resistance for Unprecedented $^{99}$TcO$_4^-$ Cleanup from Alkaline Nuclear Waste

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**ABSTRACT:** Direct removal of $^{99}$TcO$_4^-$ from alkaline nuclear waste is desirable because of the nuclear waste management and environmental protection relevant to nuclear energy but is yet to be achieved given that combined features of decent base-resistance and high uptake selectivity toward anions with low charge density have not been integrated into a single anion-exchange material. Herein, we proposed a strategy overcoming these challenges by rationally modifying the imidazolium unit of a cationic polymeric network (SCU-CPN-4) with bulky alkyl groups avoiding its ring-opening reaction induced by OH$^-$ because of the steric hindrance effect. This significantly improves not only the base-resistance but also the affinity toward TcO$_4^-$ as a result of enhanced hydrophobicity, compared to other existing anion-exchange materials. More importantly, SCU-CPN-4 exhibits record high uptake selectivity, fast sorption kinetics, sufficient robustness, and promising reusability for removing $^{99}$TcO$_4^-$ from the simulated high-level waste stream at the U.S. Savannah River Site, a typical alkaline nuclear waste, in both batch experiment and dynamic column separation test for the first time.

**INTRODUCTION**

The advanced nuclear fuel cycle has been considered a critical requirement for the sustainable development of nuclear energy. To date, PUREX (plutonium uranium reduction extraction) process is the most used technology that has been employed for used fuel reprocessing in commercial plants. However, it still suffers from some drawbacks, for example, the flammability of the organic solvents, the occurrence of radiation-induced solvent degradation, high construction costs, and production of considerable amounts of radioactive wastes. Therefore, new reprocessing approaches that enable the separation of fission products from actinides in a more environment-friendly and cost-effective manner should be further investigated. A new conceptual process (carbonate extraction, CARBEX) that aims to reprocess used nuclear fuel using high-alkaline carbonate media with oxidizing agents (i.e., H$_2$O$_2$) is considered as an alternative way of PUREX in nuclear fuel management. Additionally, unlike the acidic stream in PUREX process, the alkaline nature of CARBEX process makes it a good choice for the management of alkaline high-level radioactive waste (HLW). On the other hand, it has been estimated that ~18 000 m$^3$ of alkaline HLW are stored in Mayak Production Association and millions of gallons of alkaline HLW are stored in Hanford Site, Washington State, and Savannah River Site (SRS), South Carolina, U.S.A. most of which are leftover by the cold war and are still stored in underground tanks awaiting pretreatment and safe disposal. A crucial challenge to conquer is how to efficiently separate fission products under highly alkaline conditions. $^{99}$Tc mainly presents as a soluble pertechnetate anion ($^{99}$TcO$_4^-$) in aerobic conditions because of its noncomplexing nature and low charge density. This makes the depth removal of $^{99}$TcO$_4^-$ difficult by the precipitation method. In addition, $^{99}$TcO$_4^-$ can easily migrate into the environment via groundwater during long-term storage. Moreover, the volatile nature of Tc(VII) complexes brings higher risk of leakage during waste vitrification. In fact, Tc-99 has been leaked to the subsurface environment of several HLW storage sites, resulting in serious contamination of underground water, seawater, and rivers. Thus, it is highly desirable to seek an effective strategy for $^{99}$TcO$_4^-$ removal from highly alkaline conditions. However, this task still represents a challenge given the harsh conditions of strong...
ionizing fields (β, γ, neutron irradiations, and so forth), high salinity, and super alkalinity in alkaline nuclear wastes.

Up to now, a series of cationic materials have been evaluated for $^{99}\text{TcO}_4^-$ removal.\textsuperscript{16–21} Cationic inorganic materials, such as layered double hydroxides (LDHs),\textsuperscript{22} Yb$_3$O(OH)$_6$Cl,\textsuperscript{23} and NDTB-1,\textsuperscript{24,25} have the advantages of easy preparation and low costs but possess low capture capacity and poor selectivity toward $^{99}\text{TcO}_4^-$, which hinders their applications in actual alkaline nuclear waste streams since the concentrations of coexisting competing anions (NO$_3^-$, SO$_4^{2-}$, CO$_3^{2-}$, and OH$^-$) are several orders of magnitude higher than $^{99}\text{TcO}_4^-$. Commercially available resins (Puroilte A530E and A532E) exhibit excellent sorption selectivity toward $^{99}\text{TcO}_4^-$,\textsuperscript{26} but the slow sorption kinetics and poor radiation resistance are unavoidable issues. Cationic metal–organic frameworks (MOFs) with exchangeable anions have been widely investigated in the capture of $^{99}\text{TcO}_4^-$ recently by virtue of their high radiation resistance and excellent sorption selectivity,\textsuperscript{27–31} but the relatively weak coordination bonds perform poorly under highly alkaline conditions, thus resulting in the collapse of the cationic framework. Therefore, there is a crucial need for the development of alkaline-stable sorbent for $^{99}\text{TcO}_4^-$ removal in super alkaline nuclear wastes.

The recently developed cationic polymeric networks (CPNs) with cationic functional quaternary ammonium groups (QAs) have been proposed as a promising material for $^{99}\text{TcO}_4^-$ remediation in HLWs.\textsuperscript{32–35} The versatile functionalization of CPNs enables task-specific optimization at the molecular level to design adsorbents for envisioned functions.\textsuperscript{36,37} With ordered porosity and long-range frameworks, CPNs share similar virtues of MOFs including fast sorption kinetics and excellent sorption selectivity. More importantly, compared with MOFs, the strong covalent bonds and the nature of no heavy metal ions render CPNs a clear superiority in hydrolytic stability and sorption capacity. In addition, large conjugated modules in CPNs stabilize radical intermediates generated during the irradiation, resulting in superior anti-irradiation stability over traditional anion-exchange resins. Those superior properties make CPNs the most promising materials for the management of acidic HLWs. However, CPNs also suffer from poor alkaline stability since the cationic QAs can be easily destroyed by OH$^-$.\textsuperscript{38–40} The rational design of CPNs conjugating with high alkaline resistance is therefore a key issue.

Inspired by the recent work that installing adjacent bulky groups at C2, C4, and C5 position of imidazolium moiety can shield the nucleophilic attack from OH$^-$,\textsuperscript{41–43} we envision that this approach matches the goal of improving the alkaline resistance of CPNs and can be extended to the field of alkaline nuclear waste management. Along with this idea, a new alkaline-stable imidazolium-based CPN, namely SCU-CPN-4 (SCU = Soochow University), was constructed by the installation of bulky groups at N1, C2, N3, C4, and C5 position of imidazolium. This elaborately tailored SCU-CPN-4 not only reserves all the virtues of reported cationic CPNs in $^{99}\text{TcO}_4^-$ removal but also substantially overcomes the disadvantage of poor alkaline stability, meeting all the qualifications required in remediation of $^{99}\text{TcO}_4^-$ from the actual alkaline nuclear waste.

![Figure 1](https://doi.org/10.1021/acscentsci.1c00847)
Sorption isotherm of SCU-CPN-4 for ReO$_4^-$ in sodium chloride solution three times to completely swap out performed by immersing SCU-CPN-4-I powders into saturated energy. As shown in Figure 1b, a 2,4,5-trisubstituted imidazole-polycondensation of 1,3,5-tris(p-formylphenyl)benzene (TFP) with 1,4-bisbenzil based on a mechanism of multicomponent reaction of SCU-PN. After deprotonation and quaternization reaction of SCU-MPN with CH$_3$I. In addition, the peak at 20 mg of SCU-CPN-4 into 20 mL of aqueous solutions containing 0.15 mmol/L and m$_{sorbent}$/V$_{solution}$ = 1 g/L. (b) Sorption isotherm of SCU-CPN-4 for ReO$_4^-$ uptake. Condition: [Tc/Re]$_{initial}$ = 0.15 mmol/L and m$_{sorbent}$/V$_{solution}$ = 1 g/L and contact time = 2 h. (c) Effect of excess competing NO$_3^-$ ions on ReO$_4^-$ uptake by SCU-CPN-4. Condition: [Re]$_{initial}$ = 28 ppm, m$_{sorbent}$/V$_{solution}$ = 1 g/L and contact time = 2 h. (d) Comparison of the selectivity toward ReO$_4^-$ by various sorbents in the presence of 100-fold excess of NO$_3^-$ ions. Effect of excess competing SO$_4^{2-}$ ions on ReO$_4^-$ uptake by SCU-CPN-4. Condition: [Re]$_{initial}$ = 14 ppm, m$_{sorbent}$/V$_{solution}$ = 1 g/L and contact time = 2 h. (f) Comparison of the selectivity toward ReO$_4^-$ by various sorbents in the presence of 1000-fold excess of SO$_4^{2-}$.

**RESULTS AND DISCUSSION**

To improve the alkaline stability of the sorbent for $^{99}$TcO$_4^-$ removal in alkaline HLW streams, an alkaline-stable cationic imidazole group was designed through introducing several bulky groups to N1, C2, N3, C4, and C5 positions of imidazole to enhance alkaline resistance by steric hindrance protection (Figure 1a and Figure S1). To improve the radiation stability, conjugated phenyl groups are used to substitute the H atoms on C2, C4, and C3 positions. Besides, the total substitution around imidazolium parts by bulky groups also highly increases the overall hydrophobicity of CPN, which is beneficial to the selectivity toward ReO$_4^-$ with relatively low hydration energy. As shown in Figure 1b, a 2,4,5-trisubstituted imidazole-based polymeric network (SCU-PN) was constructed by the polycondensation of 1,3,5-tris(p-formylphenyl)benzene (TFP) with 1,4-bisbenzil based on a mechanism of multicomponent reaction of imidazole. Subsequent deprotonation and quaternization reactions with methyl iodide were carried out at imidazole moieties successively to introduce ion-exchange sites, yielding the tailored 1,2,3,4,5-pentasubstituted cationic polymeric network (SCU-CPN-4). To further circumvent the perniciousness of I$^-$ to the environment, ion exchange was finally generating SCU-CPN-4 (Figure S2). TEM-EDS mapping also confirms the nearly total exchange of I$^-$ by Cl$^-$ (Figure S6). The chemical structure SCU-PN and SUC-CPN-4 was elaborated by solid-state $^{13}$C NMR spectroscopy. As shown in Figure S3, the characteristic peaks of carboxyl $^{13}$C in 1,4-bisbenzil and the aldehyde $^{13}$C in TFP located in the range of 180.0–200.0 ppm disappear after the polycondensation between TFP and 1,4-bisbenzil, accompanied by the formation of the characteristic peak of carbon bonded to the nitrogen atom of imidazole at 146 ppm, confirming the successful construction of SCU-PN. The deprotonation process from SCU-PN to SCU-MPN was verified by the appearance of a new peak at 34.8 ppm that belongs to the methyl group. The increased relative intensity of methyl peak at SCU-CPN-4 demonstrates the occurrence of the quaternization reaction of SCU-MPN with CH$_3$I. In addition, the peak at 970 cm$^{-1}$ in Fourier transform infrared (FT-IR) spectrum corresponds to the characteristic peak of imidazole species (Figure S4), further indicating the successful construction of SCU-PN. After deprotonation and quaternization reaction with methyl iodide (CH$_3$I), the characteristic peak of imidazole species in the FT-IR spectrum changed from 970 to 1017 cm$^{-1}$, attributing to the decrease of conjugation induced by the introduction of a methyl species.

The initial sorption experiment was executed by immersing 20 mg of SCU-CPN-4 into 20 mL of aqueous solutions containing 0.15 mmol/L of $^{99}$TcO$_4^-$ or ReO$_4^-$ (nonradioactive surrogate of $^{99}$TcO$_4^-$). The effect of contact time of $^{99}$TcO$_4^-$ with SCU-CPN-4 has been evaluated by monitoring the time-dependent radioactivity through liquid scintillation counting (LSC) of the mixed solution. The kinetics data depicted in Figure 2a show that the $^{99}$TcO$_4^-$ could be rapidly adsorbed by SCU-CPN-4 and the sorption equilibrium was reached in 1
min with the removal rate as high as 99%. We assume that the fast exchange kinetics may derive from its smaller particle size, high positive charge density, and the increased hydrophobicity induced by the total substitution of imidazolium part. Remarkably, the sorption kinetics of SCU-CPN-4 is comparable to the record-holding SCU-CPN-133 and much more rapid than most of the reported sorbents (Table S1). For instance, the commercial anion-exchange resins, Purolite A532E and A530E, were reported to take as long as 120 min to reach sorption equilibrium,26 the removal rate of inorganic material NDTB-1 was only 72% after 36 h of sorption24,25 even for the crystalline cationic MOFs SCU-10346 and SCU-101,31 which own ordered pore channels, the sorption equilibrium was reached in at least 5−10 min. This significant advantage makes SCU-CPN-4 more attractive for emergency management of high-level radioactive waste, as it can provide a rapid emergency response to reduce the potential risk caused by accidental leakage of $^{99}$TcO$_4^-$.

Given the high radioactivity of $^{99}$TcO$_4^-$ required for the following batch anion-exchange experiments, nonradioactive ReO$_4^-$ was used as a surrogate for chemical behavior. Additionally, the feasibility was also confirmed by the sorption kinetics study performed on ReO$_4^-$, which is almost identical to that of $^{99}$TcO$_4^-$ (Figure 2a). The sorption kinetics of SCU-CPN-4 at a low solid/liquid ratio was carried out to further quantify the uptake kinetics. As Figure S5a shows, it takes about 25 min to reach the sorption equilibrium at a solid/liquid ratio of 0.2 g/L. Besides, the sorption data can be well fitted by the Pseudo-second-order model (Figure S5 and Table S2).

On account of the large inventory of $^{99}$TcO$_4^-$ in used nuclear wastes, sorption capacity is one of the most important parameters to evaluate the performance of adsorbents. The higher removal capacity is of great significance to increasing removal efficiency and subsequently reducing the generation of secondary waste. The isothermal sorption experiments were carried out to evaluate sorption capacity by exposing SCU-CPN-4 to ReO$_4^-$ solutions with different initial concentrations. As Figure 2b and Table S3 shows, the sorption capacity as a function of equilibrium concentration is well fitted with the Langmuir model ($R^2 > 0.98$), indicating a monolayer sorption mechanism. The maximum sorption capacity is calculated to be 437 mg/g, which is much higher than most of the reported sorbents including NDTB-1 (49.4 mg/g),27 LDHs (130.2 mg/g),27 NZVI/rGOs (85.77 mg/g),47 ZBC (25.92 mg/g),48 4-ATR resin (354 mg/g),49 D318 resin (351 mg/g),50 SCU-101 (217 mg/g),51 SCU-102 (291 mg/g),29 and SCU-103 (318 mg/g)46 (Table S4). Besides, the total exchange of Cl$^-$ by ReO$_4^-$ is also demonstrated by TEM-EDS mapping (Figure S6).

Given the presence of a huge excess of competing anions in HLW streams, especially for NO$_3^-$ and SO$_4^{2-}$, which generally exist in excess of 100−6000 folds, we then evaluated the sorption selectivity of SCU-CPN-4 for ReO$_4^-$ over NO$_3^-$ and SO$_4^{2-}$. As shown in Figure 2c, the removal efficiencies of SCU-CPN-4 toward ReO$_4^-$ are negligibly influenced by the molar ratios of 1 and 10 (NO$_3^-$/ReO$_4^-$). Even the amount of NO$_3^-$ is in a 100-fold excess, the removal percentage of ReO$_4^-$ is still as high as 91.5%, which is notably superior to most of the reported sorbents such as SCU-101 (54.4%),53 SCU-100 (73%),27
SCU-CPN-2 (79%),\textsuperscript{36} and SCU-103 (88%)\textsuperscript{46} (Figure 2d). Impressively, for the SO$_4^{2-}$ anion, which is highly competitive due to its high charge density, the removal rates of ReO$_4^{-}$ remain at a high quantitative value of 98.7% even though the amount of SO$_4^{2-}$ is in a 1000-fold excess (Figure 2e). As comparison, the removal rates by SCU-CPN-2,\textsuperscript{36} SCU-CPN-1,\textsuperscript{33} SCU-101,\textsuperscript{31} and SCU-103\textsuperscript{46} at the same condition are only 29.7%, 70%, 83% and 89.2%, respectively (Figure 2f). In addition, the $K_d$ value of SCU-CPN-4 is as high as $1.5 \times 10^7$ mL/g, significantly higher than those of other reported sorbents including NDTB-1 (652),\textsuperscript{27} LDHs (262),\textsuperscript{27} Purolite AS20E (7.6 x 10$^5$),\textsuperscript{26} SCU-102 (5.6 $\times 10^5$),\textsuperscript{33} and SCU-CPN-1 (6.2 x 10$^5$)\textsuperscript{33} (Table S5). Such excellent selectivity originates from the total substitution around imidazolium parts by bulky groups, which highly increases the overall hydrophobicity of SCU-CPN-4 and therefore the enhancement of the affinity for less hydrated $^{99}$TcO$_4^{-}$/ReO$_4^{-}$. These extraordinary characteristics make SCU-CPN-4 a potential candidate for $^{99}$TcO$_4^{-}$ remediation in HLW streams with high ionic strengths.

Considering the strong ionizing field ($\beta$, $\gamma$, and neutron irradiations, and so forth) in HLW streams, the radiation resistance of sorbents is critically required for practical applications. Very impressively, the FT-IR spectra of SCU-CPN-4 after 100 and 200 kGy of $\beta$-irradiation are almost identical to that of the pristine sample. In addition, ion exchange experiments also suggest no decrease in the ReO$_4^{-}$ uptake capacity of SCU-CPN-4 after 100 and 200 kGy of $\beta$- or $\gamma$-irradiation (Figure 3a,b). The conjugated structure plays an

Figure 4. (a) Dynamic sorption column analysis of SCU-CPN-4. Blue: sorption process, [Re]$_{\text{initial}}$ = 28 ppm, $m_{\text{sorbent}}$ = 100 mg, flow rate = 2 mL/min. Red: desorption process, $C_0$(NaCl) = 2 mol/L and flow rate = 5 mL/min. (b) Photo of the auto solid-phase extraction system (SepathsUP4). (c) Dynamic sorption column analysis of SCU-103, (d) SCU-CPN-1, and (e) SCU-CPN-2. Condition: [Re]$_{\text{initial}}$ = 28 ppm, $m_{\text{sorbent}}$ = 100 mg and flow rate = 2 mL/min. (f) Comparison of removal of ReO$_4^{-}$ by various sorbents under the condition of simulated Hanford waste. (g) Reversibility of SCU-CPN-4 under the condition of simulated SRS waste. Condition: $m_{\text{sorbent}}/V_{\text{solution}}$ = 40 g/L and contact time = 2 h. (h) Dynamic sorption column analysis of SCU-CPN-4 under the condition of simulated SRS HLW waste stream. Condition: $m_{\text{sorbent}}$ = 300 mg and flow rate = 1.35 mL/min.
important role in maintaining radiation stability by protecting the key imidazolium moieties from being degraded. As a useful comparison, the commercial resin Purolite A530E resin has been reported to exhibit excellent sorption performance for TcO$_4^-$, however, the poor radiation stability leading to a gradual decrease in sorption capacity with the increase of exposed radiation dosage is the main drawback that limiting its practical application.\textsuperscript{38} These results demonstrate that SCU-CPN-4 possesses a distinct advantage in the long term treatment of HLW streams. To validate the alkaline resistance of SCU-CPN-4, we first assessed the sorption property under different pH values. As shown in Figure 3c, a negligible decrease in the removal efficiency was observed within a wide pH range of 2 to 12. Even under the condition of 1 M NaOH solution, SCU-CPN-4 can still remove more than 98% of ReO$_4^-$ at a solid–liquid ratio of 1 g/L. More impressively, SCU-CPN-4 is fully reusable under such an alkaline environment (Figure 3d). Even after six cycles of sorption/desorption, the removal efficiency of SCU-CPN-4 toward ReO$_4^-$ still retains a high value of 98%. We further evaluated ReO$_4^-$ sorption performance of SCU-CPN-4 after being exposed to 1 M NaOH solution for 24 h. As depicted in Figure 3e,f, the FT-IR spectrum of alkali-treated SCU-CPN-4 remains almost identical to that of the original samples and the sorption capacity is not affected. In comparison, the sorption capacities of SCU-CPN-1 and SCU-CPN-2 without steric protection decrease from 953 to 350 mg/g and from 1308 to 429 mg/g, respectively. Even for SCU-103 which was reported to be more relevant to practical applications, were further performed with great practicability for $^{99}$TcO$_4^-$ (Figure 4c) and SCU-CPN-2 without steric protection (Figure 4d). Even for SCU-CPN-4 under extremely alkaline conditions. 100 mg more relevant to practical applications, were further performed with great practicability for $^{99}$TcO$_4^-$ (Figure 4c). For the first time, we performed column sorption tests on SCU-CPN-4 using simulated SRS HLW stream. As shown in Figure 4h, the ion-exchange chromatographic column filled with 300 mg of SCU-CPN-4 could remove nearly all the ReO$_4^-$ from the first 40 mL of SRS HLW waste solution, initially exhibiting the high removal efficiency toward ReO$_4^-$. These virtues demonstrate the powerful application potentials of SCU-CPN-4 in the direct removal of TcO$_4^-$ from highly alkaline wastes like SRS waste.

The sorption mechanism can be well investigated by TEM-EDS, FT-IR spectra, and XPS analysis. As probed by TEM-EDS mapping (Figure S6), the signal of Cl$^-$ disappears with the concomitant appearance of the ReO$_4^-$ in SCU-CPN-4-Re, intuitively revealing the complete ion-exchange process during the sorption. The new peaks at 896 cm$^{-1}$ in FT-IR spectrum SCU-CPN-4-Re correspond to the characteristic peaks of Re–O i $\nu_3$ asymmetric stretch, indicating ReO$_4^-$ was adsorbed into SCU-CPN-4 after the sorption process (Figure 5a). In XPS analysis, the new peaks for Re 4f, Re 4d, and Re 4p arise in SCU-CPN-4-Re at 46, 265, and 452 eV accompanied by the disappearance of Cl 2p peak (197 eV), further indicating the ion-exchange mechanism (Figure 5c). Furthermore, the Re 4f core-level spectra in SCU-CPN-4-Re was in accord with that of ReO$_4^-$. This indicated that the Re species remain unchanged during the ion-exchange process (Figure 5d).

DFT calculations were performed to investigate the mechanisms of the remarkable alkaline-stability of SCU-CPN-4 and the superior separation capability of SCU-CPN-4 toward TcO$_4^-$. Two typical fragments of SCU-CPN-4 and SCU-CPN-1 that contain their foremost structural features are selected as the theoretical models (abbreviated as M$^+$ and M$^{3+}$, respectively). First, we studied the electrostatic potential (ESP)
of M+ (up) and M** (down), as shown in Figure 6a. It can be seen that the electron density van der Waals surface near the imidazole rings shows a relatively concentrated positive ESP distribution. The ESP maxima near the imidazole ring of M+ and M** fragments. ΔG represents the solvation energy. (b) The superimposed structures of M+ fragment during 2000 fs trajectory. The structures are extracted every 4 fs. (c) Optimized structures of M:NO3−, M:SO42−, and M:TeO42−. ΔH represents the enthalpy change.

charged imidazole ring and the negative charged OH− anion. Second, the calculated solvation energies (ΔG_{solv} = −36.69 and −40.85 kcal/mol for M+ and M**) shows the installation of the bulky groups can effectively improve the hydrophobicity of M+ fragment. This result can be expected since both benzene and methyl are typical hydrophobic functional groups. We believe that the hydrophobicity enhancement of M+ is another important factor to enhance the alkaline-stability of SCU-CPN-4, since the OH− anion is extremely hydrophilic (calculated value of −370.7 kcal/mol).51 Third, the geometric fluctuations of M+ fragment were studied by means of molecular dynamics (MD) simulation. Five hundred M+ structures extracted from MD simulation trajectory are superimposed and presented in Figure 6b. It shows that the imidazole ring can be effectively encapsulated by the benzene and methyl groups since thermal motion indicates that the benzene and methyl groups can provide a certain degree of additional physical protection for the central imidazole ring. This can further assist the alkaline stability of SCU-CPN-4 because of the steric effect. In short, we conclude that the cooperation of the ESP reduction, the hydrophobicity enhancement, and the additional steric effect effectively enhance the alkaline stability of SCU-CPN-4.

Batch experiments manifest that SCU-CPN-4 exhibits excellent sorption selectivity for TeO42− under the coexistence of NO3− or SO42−. To reveal the basis for this excellent selectivity, structures of M:TeO42−, M:SO42−, and M:TeO42− and their corresponding ΔH values were optimized. As Figure 6c shows, all the negatively charged anions adsorbed on the positively charged imidazole ring. Despite showing quite similar sorption sites on M+, their corresponding ΔH values are distinctly different. The calculated ΔH values for M:TeO42− is −15.08 kcal/mol being 2 and 10 times higher than those for M:NO3− (−8.44 kcal/mol) and M:SO42− (−1.50 kcal/mol), respectively. This indicates that TeO42− is more energetically favorable than NO3− and SO42− to bind to the M+ fragment. This is mainly attributed to TeO42− which is relatively more hydrophobic than other anions. The hydration-free energy of TeO42− is −351 kJ/mol, much lower than that of NO3− (−306 kJ/mol) and SO42− (−1090 kJ/mol).52 This leads to high ΔH values for M:TeO42− and the exceptional selectivity of SCU-CPN-4 for TeO42− uptake.

### CONCLUSIONS

In summary, an alkaline-stable cationic polymeric network material (SCU-CPN-4) was rationally designed by the installation of superhydrophobic steric hindrance at the key imidazolium moiety for alkaline nuclear waste management. The elaborately tailored SCU-CPN-4 enjoys the merits of high alkaline resistance that benefits from the bulky steric hindrance as well as the excellent selectivity toward TeO42− as a result of enhanced hydrophobicity. Our study demonstrates the unexceptionable sorption properties of SCU-CPN-4 including fast sorption kinetics, high sorption capacity, excellent sorption selectivity, full reusability, and splendid sorption performances under highly alkaline aqueous solution. Moreover, the dynamic sorption performance under alkaline SRS HLW Stream reported for the first time, coupled with the splendid alkaline-resistance ability and full reusability, endow the SCU-CPN-4 with the feasibility for practical use. On the basis of these remarkable features, the newly designed steric-protected CPN holds vast potential in efficient removal of TeO42− from alkaline nuclear waste, offering a new clue to
address the long-term challenges in the CARBEX process and alkaline nuclear waste management.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscentsci.1c00847.

Experimental details including synthesis procedure, sorption procedure, and calculation methods; tables including sorption results, composition of Hanford Low Activity Waste Melter Recycle Stream and composition of Savannah River Site High-Level Waste Stream; figures including NMR spectra, FT-IR spectra, and SEM spectra (PDF)

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**Notes**

The authors declare no competing financial interest.

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