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Selective Cs-removal from highly acidic spent nuclear fuel solutions

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Abstract: Thirty liters of highly acidic spent nuclear fuel solutions need to be disposed at the “Hot Laboratory (hotlab)” facility in Paul Scherrer Institut (PSI), Switzerland. In order to significantly reduce the γ dose rate before proper disposal treatment, ^{137}Cs must be removed. In the here presented sub-project, the ion-exchange method was evaluated. Two promising sorbents, CLEVASOL® and AMP (ammonium molybdophosphate), and two derived products AMP_PAN (AMP immobilized in polyacrylonitrile) and AMP/SiO₂ (AMP immobilized on silica gel) were tested by the batch method using model solutions of important high-yield fission products (Cs, Eu, Zr, Ru, Pd and Ag), as well as U and Pu. The results showed that AMP, AMP/SiO₂ and AMP_PAN have higher selectivity for Cs than CLEVASOL® in 0.1–8 M (mol/L) HNO₃ solutions. 4 M HNO₃ solution was identified as the most suitable condition for Cs-removal with AMP, AMP_PAN and AMP/SiO₂ due to the still sufficiently high separation factor of Cs from other metal ions and an acceptable volume increase factor after dilution. The follow-up kinetic studies on AMP, AMP_PAN and AMP/SiO₂ indicated that although Cs exchange on AMP and AMP/SiO₂ is faster than on AMP_PAN in the first 5 min, they all nearly reach equilibrium after 30 min of contacting time. The isotherm curves of Cs adsorption on AMP, AMP_PAN and AMP/SiO₂ in 4 M HNO₃ showed that the maximum sorption capacity of Cs is reached asymptotically. The results from Langmuir isotherm modeling agree with results from other publications.

Keywords: Cs-removal, distribution coefficient, spent fuel, ion-exchange.

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1 Introduction

Due to several previous analytical studies, a total amount of 700 g spent nuclear fuel, from Swiss nuclear power plants, were dissolved in approximately 30 liters 8–10 M HNO₃. Now they have to be conditioned for final disposal. The specific composition of these solutions varies from batch to batch. For conditioning and final cementation, these solutions should be treated in “Fixbox 3” (a new facility for the conditioning of radioactive waste) in the “Hot Laboratory” (hotlab), at Paul Scherrer Institut (PSI). However, the high γ dose rate generated by these solutions are preventing the direct treatment. Thus, a pre-separation of high-dose rate emitters is needed. The cesium isotope ^{137}Cs ($T_{1/2} = 30.08$ years) is one of the high-yield fission products from ^{235}U fission [1] and exists in these solutions in a considerable amount. Numerous Cs-removal techniques have been developed and investigated in the past, including precipitation [2], solvent extraction [3, 4] and ion-exchange [5, 6]. Ion-exchange with packed column operation has been widely used in this field due to operational simplicity. Various Ion-exchangers are synthesized to selectively remove radioactive Cs with fast exchange kinetics and high exchange capacity [7, 8]. However, most of them are not applicable in highly acidic solution. For instance, the commercially available sorbent “Cs-treat®” was decomposing already in 2 M HNO₃ in pilot studies. Two sorbents for Cs-removal, CLEVASOL® and Ammonium molybdophosphate (AMP) that are more promising to stand the harsh environment were tested in this work. A description of the entire waste treatment procedure is given in [9].

CLEVASOL®, a novel inorganic ion-exchanger, is marketed by ADePhine GmbH. This sorbent is a grey powder consisting of a microporous, inorganic, metal-free polymer [10]. It can be directly used for column operation due to its sufficiently large particle size [10]. The pilot batch tests showed that Cs has high affinity to this sorbent and the ion-exchange process reaches equilibrium within 5 min of contacting time. The titration test showed that it has a high exchange capacity of 5.4 ± 0.2 meq/g [10]. CLEVASOL® is stable in 3 M HCl at 95 °C and it still shows >90 % of its exchange capacity after receiving an integral dose of 10^7 Gy from a ^{60}Co γ source. The formed Cs salt did not decompose even by heating to 810 °C, which showed that the formed compound has a high thermal stability [10].

AMP is a yellow, crystalline inorganic compound. The molybdophosphate complex ion $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ consists of one PO_4^{3-} group surrounded by 12 MoO_3 groups, and the ammonium ions are associated with the molybdophosphate complex [11]. The exchange of ammonium ions with Cs is more preferred than for other monovalent cations in acidic medium [11, 12], which was confirmed by other researchers [13–17]. Dolezal et al. claimed that a maximum of approximately 60 % of ammonium ions can be exchanged with Cs [18], which indicates a high exchange capacity of Cs on AMP. Rao et al. demonstrated no significant effect on exchange capacity of AMP to Cs after receiving 2 MGy of dose from electron irradiation [19], suggesting a good radiation stability. The ion-exchange mechanism of Cs on AMP is known to be isomorphous exchange of Cs ions with ammonium ions in the crystal lattice [13]. Van and Smit discovered that ammonium ions can be replaced by alkali metal ions and a more stable structure is formed when exchanging with larger monovalent ions. According to Van and Smit (1958), the phosphomolybdate complex ion, $[\text{PMo}_{12}\text{O}_{40}]^{3-}$, consists of a hollow sphere formed by the 12 MoO_3 octahedra, with the PO_4^{3-} group in the center. The large cations with associated water molecules are more fitting in these spheres of negative complex ions [12]. The Cs ion is large enough to fit into these spheres to form a more stable and insoluble structure in acidic medium [20].

AMP seems to be promising in removing radioactive Cs from acidic solutions, but it is difficult to apply AMP in column operation due to its microcrystalline structure with particle sizes in the range of 1–5 μm [21]. These small particles are impervious to liquid. In order to solve this problem, AMP can be immobilized on inert supporting materials. Over the past 40 years, various approaches to immobilize AMP on an acceptable support matrix for column operation have been investigated, including alumina [22], zirconium phosphate [23], polyacrylonitrile [24–28], and porous silica gel [29–31]. Sebesta et al. developed a mechanically durable compound by binding AMP with polyacrylonitrile (PAN) [24, 25]. Other studies have successfully made use of AMP_PAN to remove radioactive Cs from laundry wastewater, seawater and acidic nuclear waste [26–28]. Others investigated the possibility to immobilize AMP on silica gel (SiO_2) to produce a more stable form. Their results showed that AMP/ SiO_2 is a potentially efficient material for Cs-removal [18, 29–31].

Within the present study, we aimed to apply the two ion-exchangers, CLEVASOL® and AMP for our specific separation task. The latter was also tested in two

different immobilized forms, AMP_PAN and AMP/ SiO_2 . The main motivation was to select the best-suited material and determine the most suitable method considering the specific boundary conditions of the high acidity of the solutions. To accomplish the task, batch tests with model solutions were conducted to evaluate the exchange properties, including distribution coefficients (K_d), separation factors ($\alpha_{A/B}$), kinetics and practical specific capacities. The “practical specific capacity” was defined by Samuelson in 1970 as “total amount of ions expressed in milliequivalents or millimoles taken up per gram of dry ion exchanger under specified conditions (should always be given together with specification of conditions)” [32]. In the study of distribution coefficients, the stock solutions containing radioisotopes (^{137}Cs , ^{152}Eu , ^{235}U , ^{238}U , ^{239}Pu) and stable metal ions (Zr^{4+} , Ru^{3+} , Pd^{2+} and Ag^{+}) were used. In the study of kinetics, the stock solutions containing either ^{137}Cs or mixture of ^{137}Cs and stable Cs were used. In the study of practical specific capacities, the stock solutions containing mixture of ^{137}Cs and stable Cs were used.

2 Experimental

Unless specially stated, nitric acid was prepared by mixing Milli-Q water (resistivity of 18 $\text{M}\Omega\text{ cm}$) and 65 % of wt. % HNO_3 (J.T. Baker). AMP_PAN was purchased from the company TRISKEM and CLEVASOL® was provided by ADePhine GmbH. All data obtained in this paper are from experiments performed in duplicates. The temperature was kept at 22 ± 1 °C.

2.1 Preparation of AMP/ SiO_2

The procedure of preparing AMP/ SiO_2 was adapted from other works [29–31] in slightly modified form. The AMP compound is known to be easily decomposed in basic solution [14] and thus ammonia solution was used to dissolve AMP with the addition of silica gel support. First, 6.9 g of AMP and 6.3 g of silica gel (pore size 150 Å, 200–425 mesh, Sigma-Aldrich) were weighed on a digital balance (Sartorius, 98648-018-34), and added into a 500 mL of container containing 175 mL of 25 % ammonia solution (J.T. Baker). This mixture was stirred overnight with a magnetic stirrer (Heidolph MR Hei-Standard) at 300 rpm. Later excessive ammonia was evaporated by heating the mixture for several hours to 70 °C with a heating plate (Heidolph MR Hei-Standard).

Afterwards, 15 mL of 6 M HNO_3 were added to the container to re-precipitate ammonium molybdophosphate (AMP). The re-precipitated AMP was successfully immobilized on the silica gel. This product was left standing in a ventilated fume hood for 2 days until dry after removing the aqueous phase by filtration with a filter paper (Whatman™). Finally, the dry AMP/SiO₂ powder was obtained and transferred into a suitable container.

2.2 Preparation of stock solutions

The stock solutions prepared for the studies were labelled as No. 1–9. Stock solutions No. 1–3 used to measure distribution coefficients were model solutions. Several elements representing high-yield fission products (Cs, Eu, Ru, Zr, Ag and Pd) [1], as well as U and Pu as matrix elements were added. The stock solution No. 1 contained trace amounts of ¹³⁷Cs and ¹⁵²Eu in different concentrations of HNO_3 (0.1–8 M). The stock solution No. 2 contained stable Zr, Ru, U and Pu in different concentrations of HNO_3 (0.1–8 M). The stock solutions No. 3 contained stable Pd and Ag in different concentrations of HNO_3 (0.1–8 M).

The stock solution No. 4 consisted of 4 M HNO_3 and trace amounts of ¹³⁷Cs.

The stock solutions labelled as No. 5–9 were prepared by dissolving a weighed amount of CsNO_3 and spiking with ¹³⁷Cs tracer in 4 M HNO_3 .

The chemicals used for the preparation of stock solutions and the concentration of solutes in stock solutions were shown in Table 1, and measurement technique and stock solution used in each study were shown in Table 2.

Table 2: The measurement technique and stock solutions used in individual study.

Experiments	Stock solution	Measurement
K_d studies	No. 1–3	Gamma detector, ICP-MS, ICP-OES
Kinetic studies	No. 4–9	Gamma detector
Practical specific capacity studies	No. 5–9	Gamma detector

3 Distribution coefficient (K_d) studies with different HNO_3 concentration

The weighed sorbent (10 mg for CLEVASOL®, AMP and AMP/SiO₂; 40 mg for AMP_PAN) and 2 mL of the stock solution were added into a 3.5 mL glass vial. These vials were immediately shaken for 4 h by a shaking machine (IKA® VIBRAX VXR basic), at 1500 rpm. Afterwards, the aqueous phase in each vial was separated from the solid phase by rapid filtration on syringe filters (0.1 µm pore size for AMP and AMP/SiO₂, Whatman™; 2 µm pore size for CLEVASOL® and AMP_PAN, Miller®). One milliliter of the separated aqueous phase and 1 mL of the corresponding stock solution were measured by γ -ray spectrometry with a high purity germanium γ detector (HPGe), or Inductively-Coupled Plasma Mass Spectrometry (ICP-MS)/Inductively-Coupled Plasma Optical Emission Spectrometry (ICP-OES) to quantify the count rate of γ emitters or the concentration of each investigated element, respectively.

Table 1: The stock solutions prepared in the studies.

Stock solution	Matrix	Content	Solute concentration	Total volume
No. 1	0.1–8 M HNO_3	¹³⁷ Cs, ¹⁵² Eu	Cs, Eu: trace amount	20 mL
No. 2	0.1–8 M HNO_3	RuCl ₃ (Fluka) ZrCl ₄ (Sigma-Aldrich) UO ₂ (NO ₃) ₂ ·6H ₂ O (Merck) Pu-239 (Hotlab sample 18)	Ru: 80 ppb Zr: 80 ppb U: 7.5 ppm Pu: 25 ppb	100 mL
No. 3	0.1–8 M HNO_3	AgNO ₃ (Sigma-Aldrich), Pd(NO ₃) ₂ ·2H ₂ O (Sigma-Aldrich)	Ag: 900 ppb Pd: 1200 ppb	50 mL
No. 4	4 M HNO_3	¹³⁷ Cs	Cs: trace amount	200 mL
No. 5	4 M HNO_3	CsNO ₃ (sigma-Aldrich), ¹³⁷ Cs	Cs: 0.1 M	50 mL
No. 6	4 M HNO_3		Cs: 0.05 M	50 mL
No. 7	4 M HNO_3		Cs: 0.03 M	50 mL
No. 8	4 M HNO_3		Cs: 0.01 M	50 mL
No. 9	4 M HNO_3		Cs: 0.005 M	100 mL

4 Kinetic studies

Two milliliter of stock solution (No. 4 or No. 9) and weighed sorbent (10 mg for AMP and AMP/SiO₂; 40 mg for AMP_PAN) were added into a 3.5 mL glass vial and these vials were shaken for different time intervals (10 s to 4 h) by a shaking machine at 1500 rpm. After reaching the preset time interval, the aqueous phase in each vial was immediately separated from the solid phase by syringe filters. The phases were separated in less than 2 s in case of <300 s contact time and within 10 s when the contacting time was 300 s to 4 h. The uncertainty of the contacting time was in a range of 0.5 %–20 %, respectively. Finally, 1 mL of the separated aqueous phase in each vial and 1 mL of stock solution were measured by means of γ -ray spectrometry to quantify the count rate of ¹³⁷Cs.

5 Practical specific capacity studies

A series of batch tests were conducted to quantify the practical specific capacity of sorbent toward Cs. Experiments were performed by contacting different sorbents with each stock solution (No. 5–9) containing different Cs concentrations. During the experiments, 2 mL of stock solution were pipetted into a 3.5 mL glass vial containing weighed sorbent (10 mg for AMP and AMP/SiO₂; 40 mg for AMP_PAN). Later, these vials were shaken by a shaking machine for 4 h at 1500 rpm. Afterwards, the aqueous phase in each vial was separated from the solid phase by syringe filters. Finally, 1 mL of the separated aqueous phase in each vial and 1 mL of stock solution were measured by γ -ray spectrometry to quantify the count rate of ¹³⁷Cs.

6 Measurement techniques

The separated aqueous phases containing ¹³⁷Cs were kept for at least half an hour to reach the ¹³⁷Cs and ^{137m}Ba radioactive equilibrium before measurement. The samples containing ¹³⁷Cs and ¹⁵²Eu were measured with a high purity germanium (HPGe) detector (Canberra EFPC 25, Gamma Analyst Canberra Lynx with software Genie2000) to identify and quantify the count rate of γ emitters. Gamma energies of 661 keV and 122 keV were used for ¹³⁷Cs and ¹⁵²Eu, respectively. Counting uncertainty (1 σ) was less than 3 % for all of the measured samples. For analyses of all active samples containing γ emitters, the same detector and the same parameters (sample geometry, position and

distance) were used for the measurements of the stock solutions and the corresponding aqueous phases after phase separation. This way, no efficiency calibration was necessary.

The samples containing Ru, Zr, U and Pu (originated from stock solution No. 2 with four sorbents) and samples containing Pd and Ag (originated from stock solutions No. 3 with CLEVASOL® and AMP/SiO₂) were measured on an Element II® Sector-Field Inductively-Coupled Plasma Mass Spectrometry (SF-ICP-MS) system produced by Thermo Fisher Scientific. The stock-solutions were diluted 1:100 and the samples were diluted between 1:3 and 1:50 with 0.28 M HNO₃. The uncertainties of the ICP-MS analysis were in the range of 1.25–14 % (1 σ).

The samples containing Pd and Ag (originated from stock solution No. 3 with AMP and AMP_PAN) were measured on Inductively-Coupled Plasma Optical Emission Spectrometry system (ICP-OES, VISTA AX, Agilent Technologies, Inc. USA). The samples were diluted 1:20 with 0.5 M HNO₃. The uncertainty of the ICP-OES analysis is less than 2 % (1 σ).

7 Uncertainty calculations

The uncertainty of different sources is shown in Table 3.

The uncertainty evaluation procedure used in this paper was to propagate each uncertainty source in experiment and the standard deviations to present the final uncertainty [33].

For example, in distribution coefficient (separation factor) experiments, the uncertainty u_{K_d} for each individual experiment was calculated by applying equation (1).

$$u_{K_d} = \sqrt{\left(\frac{\partial K_d}{\partial p_1} \Delta p_1\right)^2 + \left(\frac{\partial K_d}{\partial p_2} \Delta p_2\right)^2 + \left(\frac{\partial K_d}{\partial p_3} \Delta p_3\right)^2 + \dots} \quad (1)$$

where p_1, p_2, p_3, \dots represent the parameters in the function of K_d (e.g. solute concentration, mass of sorbent, volume of solution etc.); $\Delta p_1, \Delta p_2, \Delta p_3$ represent the absolute uncertainty of each parameter.

Table 3: The uncertainties during the experiments.

Uncertainty sources	Uncertainty (1 σ)
ICP-MS measurement	1.25 %–14 %
ICP-OES measurement	2 %
HPGe measurement	0.1 %–3 %
Pipetting	1 %
Balance	0.25 %

Since the experiment was performed twice, the standard deviation was calculated from the duplicated values.

$$\sigma = \frac{\sqrt{(\overline{K_d} - K_{d1})^2 + (\overline{K_d} - K_{d2})^2}}{\sqrt{2}} \quad (2)$$

where: K_{d1} and K_{d2} are the calculated values of distribution coefficient in each experiment; $\overline{K_d}$ is the average value of distribution coefficient from duplicated experiments.

Finally, the uncertainty of distribution coefficient (U_{Kd}) was obtained by propagating the calculated uncertainties (u) and the standard deviation (σ) of replicates.

$$U_{Kd} = \sqrt{\frac{1}{4}(u_{Kd1}^2 + u_{Kd2}^2) + \sigma^2} \quad (3)$$

The value of distribution coefficient (K_d) was presented as the average value ($\overline{K_d}$) associated with the final uncertainty.

$$K_d = \overline{K_d} \pm U_{Kd} \quad (4)$$

The same procedure of uncertainty evaluation was used for the study of kinetics and practical specific capacity.

In the study of Langmuir and Freundlich modeling, the final uncertainty of each parameter was calculated by propagating the uncertainty of every data point and the uncertainty from linear regression. The uncertainties presented within this work are stated as 1σ .

8 Results and discussion

8.1 Distribution coefficients studies

The distribution coefficient (K_d) serves as an indicator for the affinity of an ion to the sorbent under specific conditions during contact. The separation factor of an ion from other interfering ions can also be obtained. In addition, the most suitable conditions for Cs-removal can be determined by considering not only high distribution coefficients of Cs but also sufficiently low distribution coefficient of U, Pu and other interfering ions (high separation factor of Cs from other ions).

Distribution coefficients were calculated based on the following equation (5) [34]:

$$K_d = \frac{(C_{\text{initial}} - C_{\text{liquid}})}{C_{\text{liquid}}} \times \frac{V}{m} \quad (5)$$

where C_{initial} is the initial concentration of the ion (or the count rate of the radioactive ion) in solution before contacting the sorbent; C_{liquid} is the final concentration of the ion (or the count rate of the radioactive ion) in solution after contact with the sorbent; V is the volume of solution (mL); m is the dry mass of the sorbent (g).

ICP-MS/ICP-OES analysis directly determines the concentration of each isotope in the measured samples, while γ -ray spectrometry quantifies the count rate of each radioactive ion in the measured samples. Thus, the distribution coefficient of each metal ion can be calculated by equation (5).

Plots of K_d vs. HNO_3 concentration are shown in Figure 1. K_d values of all metal ions on all sorbents are largest in 0.1 M HNO_3 solution and they decrease with increasing H^+ concentration. This trend may indicate that the metal ion-exchange is inhibited due to the presence of H^+ that competes with these metal ions for the exchange sites on the sorbent [35]. The results of distribution coefficient studies on AMP, AMP/SiO₂ and AMP_PAN (Figure 1a, c and d) show that the K_d values of Cs are at least 2 orders of magnitude larger than for other metal ions in 1–8 M HNO_3 solutions. The K_d value of Cs on AMP in a wide range of HNO_3 agrees with the results of Suss [36]. The value of $K_{d(\text{UO}_2)}$ on AMP is around 20 in 0.1 M HNO_3 and decreases to around 10 in 1 M HNO_3 , which is in agreement with previous work of Ganzerlin (~20 and ~10 in 0.1 and 1 M HNO_3 , respectively) [37]. The high K_d value of Cs and low K_d value of Pu on AMP_PAN in acidic solutions agree with the values in [34]. The results of distribution coefficient studies on CLEVASOL® (Figure 1b) show that the K_d value of Eu is similar to that of Cs in 0.1 M HNO_3 solution and the K_d value of other ions are close to the value of Cs in 1–8 M HNO_3 solutions. These relatively low separation factors of Cs on CLEVASOL® toward other metal ions in 2–8 M HNO_3 solutions, makes this sorbent less favorable in highly active acidic solutions.

8.2 Separation factor studies

The way to calculate the separation factor of one ion from another one is shown as equation (6) [32].

$$\alpha_{A/B} = \frac{K_{d(A)}}{K_{d(B)}} \quad (6)$$

where:

- $\alpha_{A/B}$ is the separation factor of ion A from ion B;
- $K_{d(A)}$ is the distribution coefficient of ion A;
- $K_{d(B)}$ is the distribution coefficient of ion B.

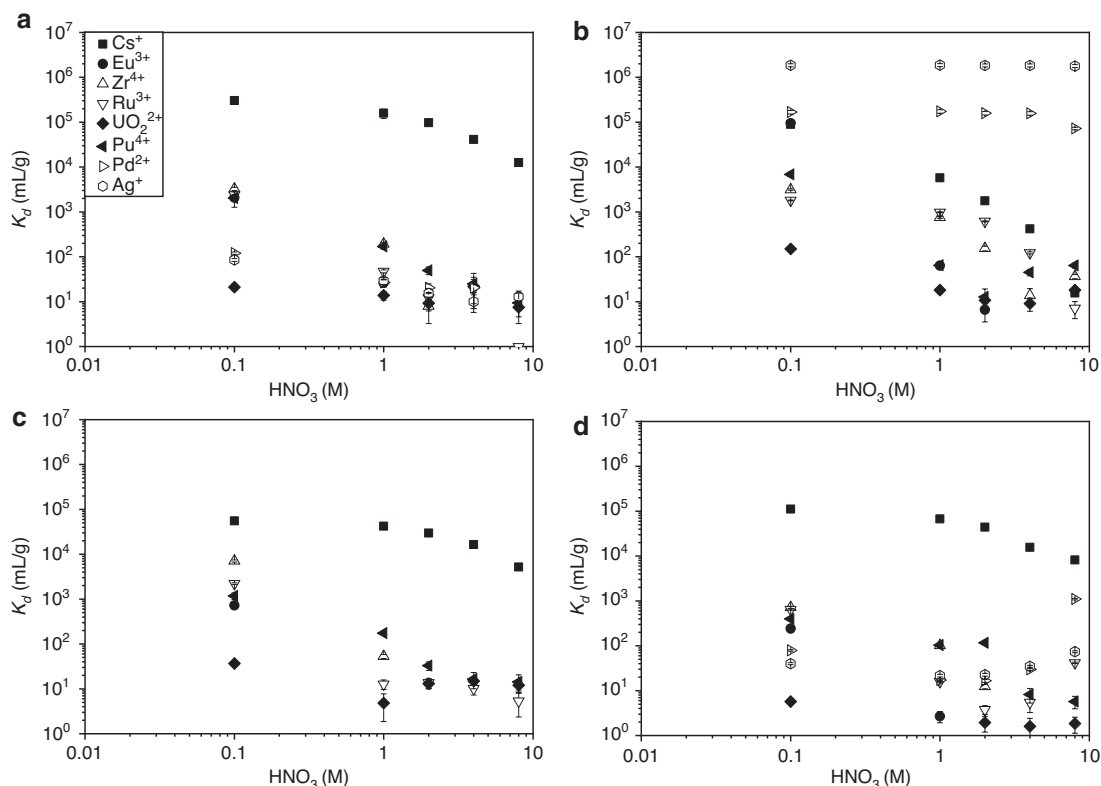


Figure 1: Distribution coefficients of different metal ions on AMP (a), CLEVASOL® (b), AMP/SiO₂ (c) and AMP_PAN (d) in different systems. The K_d value of Ag with CLEVASOL in 0.1–4 M HNO₃ and the K_d value of Pd with CLEVASOL in 0.1 M HNO₃ were given as minimum value because the concentration of Ag and Pd after adsorption was under the ICP-MS detection limit.

The separation factor of Cs from other metal ions in different systems are presented in Table 4. It is notable that the separation factors with AMP, AMP/SiO₂ and AMP_PAN system are much higher than with CLEVASOL®. This confirms that AMP, AMP/SiO₂ and AMP_PAN are more suitable

for the Cs-removal task. In the system of AMP, AMP/SiO₂ and AMP_PAN in higher acidic solutions (2–8 M HNO₃), the separation factor of Cs from most metal ions reaches a maximum in 2 M HNO₃ solution and then decreases with increasing H⁺ concentration, which implies the highest

Table 4: Separation factors of Cs from other metal in different systems.

	HNO ₃	Cs/Eu	Cs/Zr	Cs/Ru	Cs/U	Cs/Pu	Cs/Pd	Cs/Ag
AMP	2 M	>8.70E4	>6.47E3	>5.48E3	>6.80E3	>1.45E3	>3.37E3	>4.22E3
	4 M	>4.07E4	N*	>1.31E3	>1.16E3	>9.46E2	>1.58E3	>2.68E3
	8 M	>1.24E4	N*	>2.86E3	>1.13E3	>7.86E2	>1.24E4	>6.83E2
CLEVASOL	2 M	>1.66E2	<14	<4	(1.64±0.56)E2	(1.39±0.75)E2	<0.1	<0.1
	4 M	>3.96E2	<61	<4	<80	<12	<0.1	<0.1
	8 M	<19	<1	<6	<2	<1	<0.1	<0.1
AMP/SiO ₂	2 M	>2.88E4	N*	>1.63E3	>1.72E3	>7.14E2	N*	N*
	4 M	>1.58 E4	N*	>1.17E3	>8.50E2	>6.76E2	N*	N*
	8 M	>5.11E3	N*	>5.79E2	>3.26E2	>2.46E2	N*	N*
AMP_PAN	2 M	>4.18E4	(3.56±0.51)E3	>8.75E3	>1.47E4	>3.40E2	(2.65±0.30)E3	(1.94±0.19)E3
	4 M	>1.52E4	N*	>1.97E3	>5.96E3	>1.35E3	(5.27±0.39)E2	(4.46±0.30)E2
	8 M	>7.98E3	N*	>1.84E2	>2.94E3	>1.06E3	<8	(1.11±0.06)E2

N*, No available data. In 2–8 M HNO₃, some of the metal ions were barely adsorbed by the sorbent, which resulted in small values of the calculated K_d but however large uncertainty of K_d and separation factors of Cs to the element (e. g. K_d value of U on AMP_PAN in 4 M HNO₃ is 1.6±0.82 and the uncertainty of Cs/U is >50 %). Therefore, only the minimum or maximum values of separation factor were given for these elements.

separation efficiency of Cs would be reached in 2 M HNO_3 . Either neutralization (with base) or dilution (with water) is possible to decrease the H^+ concentration in the spent fuel solutions. However, the neutralization method will significantly increase the interfering ion concentration, which could influence the selectivity and the distribution coefficient of Cs on the sorbent (similar to H^+ affecting the $K_{d(\text{Cs})}$ on the sorbent) [35]. Therefore, diluting the initially 8 M HNO_3 solutions to 4 M gives the most suitable conditions in terms of fulfilling the two boundary conditions: as low as possible volume versus as high as possible separation factors.

The separation factor of Cs/Pu with AMP_PAN system is $>1.36\text{E}3$ in 4 M HNO_3 . Todd et al. report a value of $1.4\text{E}3$ in 3 M HNO_3 [34].

8.3 Kinetic studies of Cs adsorption

In Figure 2, the time dependence of the Cs absorption onto AMP, AMP/ SiO_2 and AMP-PAN from 4 M HNO_3 solution is plotted. The ratio (C/C_0) was calculated according to equation (7).

$$C/C_0 = \frac{C_{\text{initial}} - C_{\text{liquid}}}{C_{\text{initial}}} \times 100\% \quad (7)$$

where: C_{initial} is the count rate of ^{137}Cs in 1 mL of solution before contacting the sorbent (cps); C_{liquid} is the count rate of ^{137}Cs in 1 mL of solution after contacting the sorbent (cps).

The Cs exchange process in case of AMP reaches equilibrium within 10 s, which is in agreement with a previous

study [38]. The Cs exchange on AMP/ SiO_2 and AMP_PAN reaches equilibrium within 30 min. Comparing AMP and AMP/ SiO_2 , Cs exchange on AMP_PAN is slower. The value of C/C_0 increases gradually up to 300 s and then levels off from half an hour to 4 h. Cs exchange on all these sorbents can be considered as reaching equilibrium after half an hour of contact time, because no considerable change is observed of the value of C/C_0 after 30 min. The kinetics curves confirm that 4 h of contacting time is more than sufficient to reach the ion-exchange equilibrium with these sorbents in the K_d experiments. The different kinetic behavior between AMP_PAN and AMP (AMP/ SiO_2) is caused by the larger particle size and the much more compact internal structure of AMP_PAN compared to AMP and AMP/ SiO_2 , which could inhibit mass transfer during the exchange process [26].

In addition, the moving boundary model was used to identify the predominant rate-controlling step during the Cs adsorption on AMP_PAN [38–41]. The moving boundary model assumes that a sharp boundary separates a reacting shell from an unreacted core and the boundary advances toward the center of the solid during the process of adsorption [39–40].

If the adsorption process is controlled by liquid film diffusion, the following relation applies [41]:

$$-\ln(1-F) = Kt \quad (8)$$

If the adsorption process is controlled by ion diffusion in the solid phase, the equation used is:

$$1 - 3(1-F)^{2/3} + 2(1-F) = Kt \quad (9)$$

If the adsorption process is controlled by chemical reaction, the following equation is used:

$$1 - (1-F)^{1/3} = Kt \quad (10)$$

where: F is the fractional attainment of equilibrium adsorption (the ratio of adsorbed Cs content on the sorbent at each time point to the adsorbed Cs content on the sorbent at equilibrium); K is the kinetic coefficient or rate constant (s^{-1}); t is the contacting time (s)

In Figure 3c, the Kt values obtained applying the three adsorption models (eqs. 8–10) in dependence of the time are shown, as well as the corresponding linear regression coefficients R^2 .

In Figure 3a, the value of C/C_0 increases only slightly from 300 s to 1800 s. By taking the results shown in Figure 2 into consideration, it can be assumed that Cs adsorption reached equilibrium after 1800 s of contacting time in this experiment. After testing these three models for Cs adsorption on AMP_PAN, as shown in

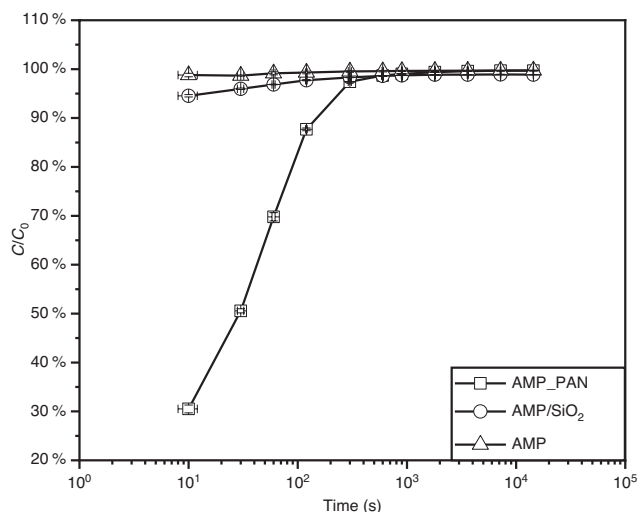


Figure 2: Kinetic studies of Cs exchange on sorbents with No. 4 stock solution.

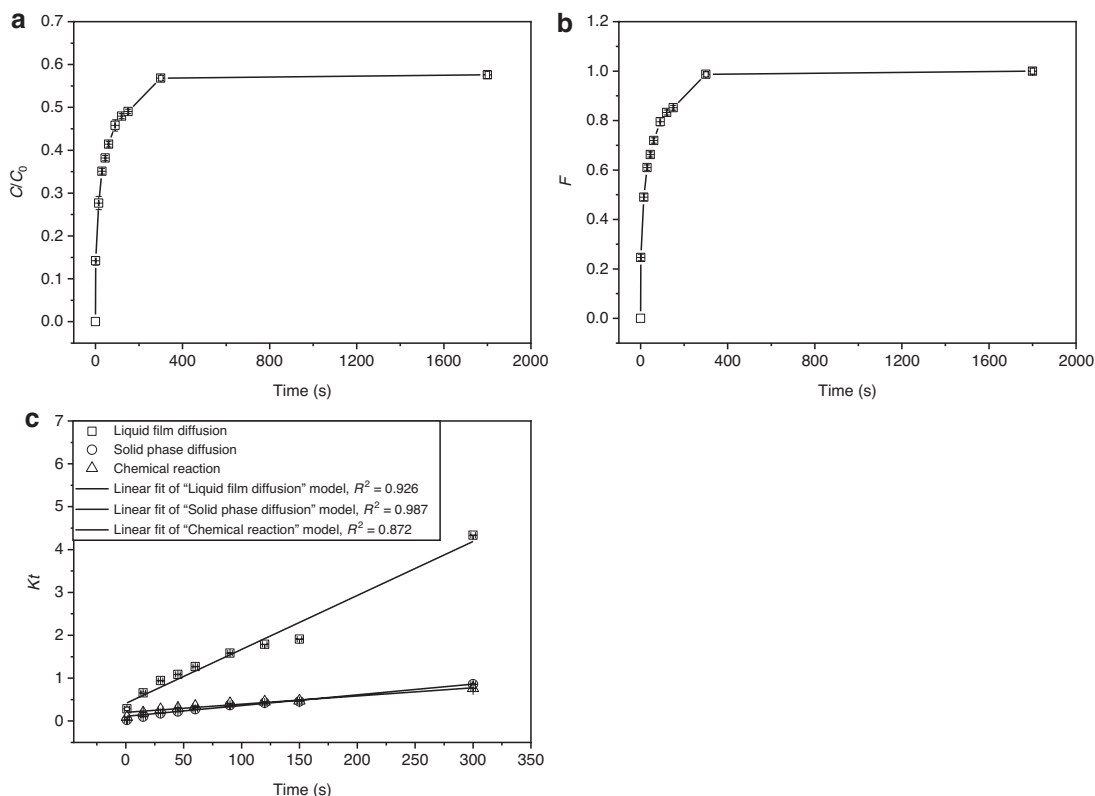


Figure 3: Kinetic studies of Cs adsorption and simulations.

(a) Kinetic studies of Cs adsorption on AMP_PAN with No. 9 stock solution. (b) Rate of Cs adsorption on AMP_PAN. (c) Plots of Eq. (8–10) for Cs adsorption on AMP_PAN.

Figure 3c, the best fitting model with the highest R^2 value (0.987) is the solid phase diffusion model, which indicates that the Cs exchange rate on AMP_PAN is controlled by Cs diffusion in the solid particles. This result is in agreement with the result published by Tranter et al. in 2002 [42].

8.4 Practical specific capacity studies

The practical specific capacity is expressed as the total amount of ions in gram or milligram taken up per gram of dry sorbent under specified conditions [32]. In our batch experiments, a series of tests were conducted at fixed experimental conditions (temperature, solution acidity, sorbent concentration, etc.) with different solute concentrations. The results were evaluated by the theoretical models to describe the exchange capacity of sorbent to solute and the adsorption features in our solid-liquid systems. The Langmuir and Freundlich models are well-known models to analyze the experimental data to determine the maximum adsorption content and the adsorption features [43].

After the count rate of ^{137}Cs was quantified in each sample and stock solution, the practical specific capacity

of sorbent toward Cs was calculated by the following equation [42]:

$$[M_{\text{solid}}] = \frac{(C_{\text{initial}} - C_{\text{liquid}})}{C_{\text{initial}}} \times \frac{[M_{\text{Cs}}] \times V}{m} \quad (11)$$

where: $[M_{\text{solid}}]$ is the practical specific capacity (g Cs/g sorbent); C_{initial} is the count rate of ^{137}Cs in 1 mL of solution before contacting with the sorbent (cps); C_{liquid} is the count rate of ^{137}Cs in 1 mL of solution after contacting with the sorbent (cps); $[M_{\text{Cs}}]$ is the concentration of Cs in the initial solution before contacting with the sorbent (g/L); m is the mass of dry sorbent before contacting with the initial solution (g); V is the volume of the stock solution in the solid-liquid system (L).

The isotherms are presented in Figure 4 by plotting the practical specific capacity of sorbent toward Cs against the equilibrium Cs concentration $[Cs]_{\text{eq}}$ in aqueous phase (g/L). As shown in Figure 4, the practical specific capacity increases with Cs concentration in the initial solution and gradually reaches a maximum under our specific experimental conditions.

In order to analyze the experimental data, Langmuir and Freundlich isotherm models are used here. The

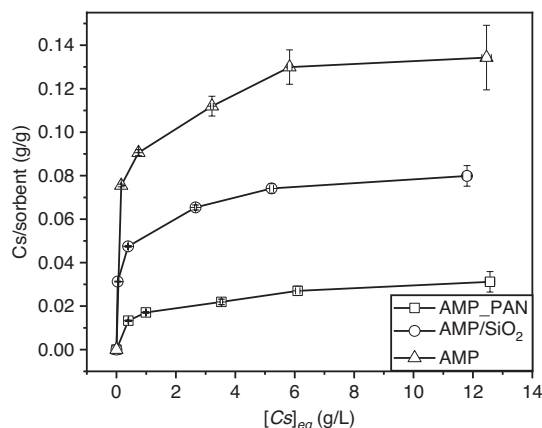


Figure 4: Amount of exchanged Cs per gram of sorbent against equilibrium Cs concentration in the liquid phase at 22 °C, after 4 h contacting time.

classical Langmuir isotherm assumes that the sorbent has a homogeneous flat surface and a monolayer adsorption on the surface [43]. The surface contains a finite number of adsorption sites and no transmigration of adsorbate on the surface [44]. This implies that once all of the adsorption sites on the surface are filled, the maximum adsorption on the surface is achieved. The general mathematical form of the Langmuir isotherm model is presented as follows:

$$[M_{\text{solid}}] = \frac{Q \times K \times [Cs]_{\text{eq}}}{1 + K \times [Cs]_{\text{eq}}} \quad (12)$$

where: $[M_{\text{solid}}]$ is the same definition as before; K is the Langmuir equilibrium constant related to the energy of adsorption (L/g). Q is the maximum Cs adsorption on the solid phase (g Cs/g sorbent); $[Cs]_{\text{eq}}$ is the concentration of Cs in solution after contacting with sorbent (g/L).

The value of $[M_{\text{solid}}]$ is obtained from experimental data and the values of Q and K can be determined graphically by linearization and reformulating equation (12) [44]:

$$\frac{[Cs]_{\text{eq}}}{[M_{\text{solid}}]} = \frac{[Cs]_{\text{eq}}}{Q} + \frac{1}{K \times Q} \quad (13)$$

When $[Cs]_{\text{eq}}$ is plotted against $\frac{[Cs]_{\text{eq}}}{[M_{\text{solid}}]}$, the inverse of the slope is equal to Q and K is calculated from the slope and intercept.

A linear plot of specific adsorption $\left(\frac{[Cs]_{\text{eq}}}{[M_{\text{solid}}]}\right)$ against the final Cs concentration in the solution ($[Cs]_{\text{eq}}$) is presented in Figure 5a and the value of parameters for Langmuir model as well as the calculated capacity from linear regression are presented in Table 5. The Langmuir model fitted the experimental data very well for Cs

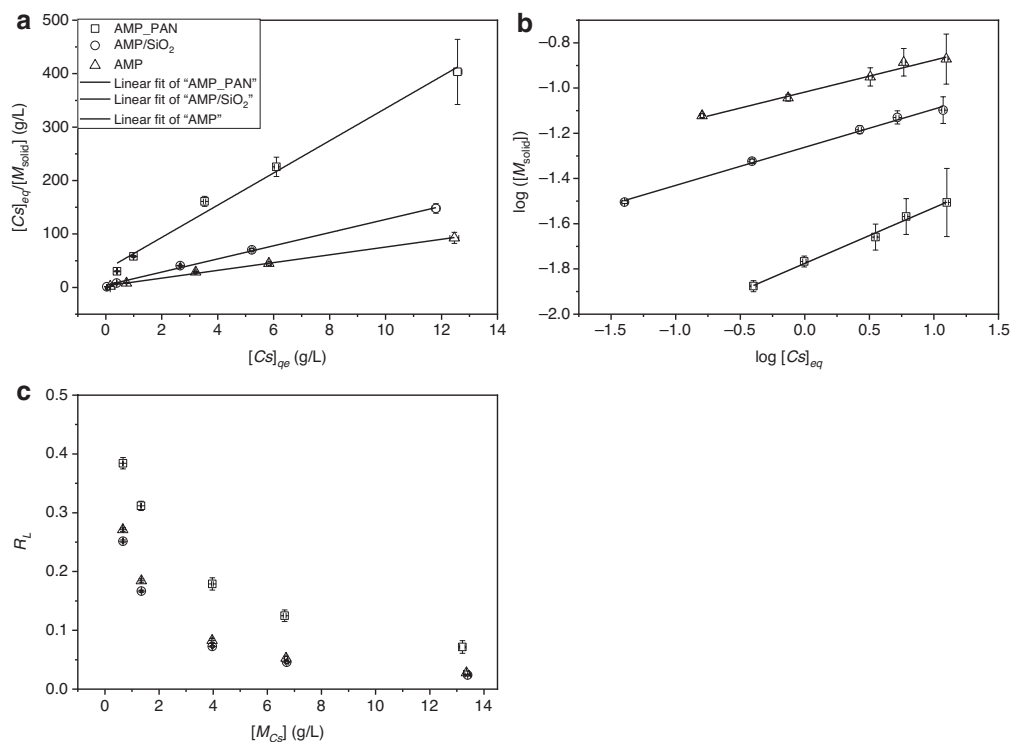


Figure 5: Simulation of Langmuir and Freundlich models.

(a) Linearized Langmuir adsorption isotherm plot for AMP_PAN, AMP/SiO₂ and AMP. (b) Linearized Freundlich adsorption isotherm plot for AMP_PAN, AMP/SiO₂ and AMP. (c) The Langmuir separation factor under various Cs adsorption conditions.

Table 5: Isotherm parameters for Cs adsorption on sorbents.

Isotherm model	Sorbent	Slope	Calculated capacity Q (g/g)	Intercept	Langmuir constant K (L/g)	R^2
Langmuir	AMP_PAN	30.2 ± 1.7	$(33.2 \pm 6.5)E-3$	33.3 ± 11.1	0.9 ± 0.5	0.987
	AMP/SiO ₂	12.3 ± 0.3	$(81.2 \pm 7.2)E-3$	4.1 ± 2.0	3.0 ± 2.1	0.997
	AMP	7.3 ± 0.2	$(137.8 \pm 19.7)E-3$	2.9 ± 1.0	2.5 ± 1.5	0.998
	Sorbent	Slope	Freundlich constant n	Intercept	Freundlich constant A	R^2
Freundlich	AMP_PAN	0.25 ± 0.01	4.1 ± 0.8	(-1.78 ± 0.01)	$(16.8 \pm 3.1)E-3$	0.991
	AMP/SiO ₂	0.17 ± 0.01	5.9 ± 0.5	(-1.26 ± 0.01)	$(54.7 \pm 4.2)E-3$	0.994
	AMP	0.14 ± 0.01	7.1 ± 1.5	(-1.02 ± 0.01)	$(96.6 \pm 19.3)E-3$	0.978

adsorption on three sorbents, the coefficient of determination, R^2 , is larger than 0.99. The calculated capacity of AMP_PAN toward Cs (33.2 ± 6.5 mg/g) is in agreement with the value (~ 33 mg/g) provided by the supplier (TRISKEM). The calculated capacity of AMP toward Cs (137.8 ± 19.7 mg/g) agrees with the published data that the maximum cesium adsorption on AMP is approximately 1 mmol/g ($125\text{--}145$ mg/g) [18, 45]. The calculated capacity of AMP/SiO₂ toward Cs is 81.2 ± 7.2 mg/g, which implies the active content of AMP in AMP/SiO₂ is larger than 50 wt.%.

One of the derived Langmuir isotherm parameters, a dimensionless constant called Langmuir separation factor (R_L), can be used to distinguish “favorable” and “unfavorable” adsorption processes [45, 46]. The “favorable” adsorption indicates that the solutes have high affinity to the sorbent and vice versa. This parameter is expressed in the following equation:

$$R_L = \frac{1}{1 + K \times [M_{Cs}]} \quad (14)$$

where: K is the Langmuir constant (L/g) and $[M_{Cs}]$ is the Cs concentration in the initial solution (g/L). If $R_L = 0$, the adsorption is irreversible; if $R_L = 1$, the adsorption is independent of solute concentration; if $R_L > 1$, the adsorption is “unfavorable”; if $0 < R_L < 1$, the adsorption is “favorable” [46, 47]. The value of R_L under different conditions is presented in Figure 5c.

Generally, the value of R_L for all of our cases of Cs adsorption lies between 0 and 0.5 in Figure 5c, which indicates a “favorable” Cs adsorption process on AMP_PAN, AMP/SiO₂ and AMP and confirms high affinity of Cs to these sorbents.

The other classical isotherm, the Freundlich model, was also applied to analyze the experimental data. This isotherm assumes that the sorbent has a heterogeneous flat surface and the mathematical form is as follows [43].

$$[M_{solid}] = A \times [Cs]_{eq}^{(1/n)} \quad (15)$$

$$\log([M_{solid}]) = \frac{1}{n} \times \log([Cs]_{eq}) + \log(A) \quad (16)$$

where: $[M_{solid}]$ and $[Cs]_{eq}$ have the same definitions as with the Langmuir isotherm; A and n are dimensionless constants that relate to the adsorption capacity and adsorption strength, respectively [48].

Similarly the values of A and n can also be determined by plotting $\log([M_{solid}])$ against $\log([Cs]_{eq})$, the slope is equal to $(1/n)$ and the intercept is equal to $\log(A)$.

The adsorption process is usually classified by the values of n : good (2–10), moderately difficult (1–2), poor (<1) [46, 49], and the Freundlich model is not effective (>10). This method is denoted as “ n ” method by Chengjun [49].

A linear plot of $\log([M_{solid}])$ versus $\log([Cs]_{eq})$ is presented in Figure 5b. The values of Freundlich parameters are calculated and presented in Table 5. The Freundlich model fitted also very well for Cs adsorption on these three sorbents with $R^2 > 0.97$. According to the “ n ” method, the Freundlich constant n for all three sorbents is in the range of 2–10, which shows good adsorption to Cs in these systems. In addition, the Freundlich constant n and A are of the order of $AMP > AMP/SiO_2 > AMP_PAN$, which indicates that the Cs adsorption intensity and adsorption capacity to Cs are both of the order of $AMP > AMP/SiO_2 > AMP_PAN$. This confirms the results of Langmuir model simulation that the adsorption capacity toward Cs is of the order of $AMP > AMP/SiO_2 > AMP_PAN$.

9 Conclusion and outlook

In the present paper, two promising sorbents CLEVASOL® and AMP and two engineered products AMP_PAN and AMP/SiO₂ are examined in order to develop a suitable and efficient system for a selective Cs-removal process from high-acidic spent nuclear fuel solutions. The results of batch experiments confirmed that the AMP system

(AMP/SiO₂ and AMP_PAN) is the better option for selective removal of Cs, and that the suitable acid concentration is 4 M HNO₃ due to the sufficiently high separation factor of Cs from other metal ions and small dilution factor for the spent fuel solutions. The kinetic study results suggest that 300 s of contacting time in the batch method is sufficient to remove the bulk of Cs from the solutions by AMP, AMP/SiO₂ and AMP_PAN, even though the equilibrium is not fully reached. The Cs adsorption process on AMP_PAN is much slower than the Cs adsorption process on AMP and AMP/SiO₂ because the Cs adsorption on AMP_PAN is a solid phase diffusion controlled process. The maximum Cs adsorption, calculated from Langmuir linear regression, on AMP, AMP/SiO₂ and AMP_PAN are 137.8 ± 19.7 mg/g, 81.2 ± 7.2 mg/g and 33.2 ± 6.5 mg/g, respectively in 4 M HNO₃. In summary, batch method tests proved that AMP, AMP/SiO₂ and AMP_PAN are very promising materials for selectively Cs-removal. The purchased AMP_PAN and lab-made AMP/SiO₂ will be further investigated in terms of column operations.

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References

1. IAEA nuclear data section. Available at: <https://www-nds.iaea.org/sgnucdat/c3.htm>. Accessed 10 July 2019.
2. Konvalova, N. A., Rumer, I. A., Kulyukhin, S. A.: Coprecipitation of ¹³⁷Cs and ⁸⁵Sr microquantities with complex compound [M(18-crown-6)]BPh₄ (M=Na⁺, Cs⁺) from neutral and alkaline solutions. *Radiochim. Acta.* **97**, 559 (2011).
3. Dash, A., Ram, R., Pamale, Y. A., Deodhar, A. S., Venkatesh, M.: Recovery of ¹³⁷Cs from laboratory waste using solvent extraction with sodium tetraphenylboron (TPB). *Sep. Sci. Technol.* **47**, 81 (2011).
4. Dozol, J. F., Dozol, M., Maclas, R. M.: Extraction of strontium and cesium by dicarbollides, crown ethers and functionalized calixarenes. *J. Incl. Phenom. Macrocycl. Chem.* **38**, 1 (2000).
5. Anthony, R. G., Dosch, R. G., Gu, D., Philip, C. V.: Use of silicotitanates for removing cesium and strontium from defense waste. *Ind. Eng. Chem. Res.* **32**, 2702 (1994).
6. Todd, T. A., Brewer, K. N., Wood, D. J., Tullock, P. A., Mann, N. R., Olson, L. G.: Evaluation and testing of inorganic ion exchange sorbents for the removal of cesium-137 from actual IDAHO Nuclear Technology and Engineering Center acidic tank waste. *Sep. Sci. Technol.* **36**, 999 (2007).
7. Mann, N. R., Todd, T. A.: Removal of cesium from acidic radioactive tank waste by using IONSIV IE-911. *Sep. Sci. Technol.* **39**, 2351 (2005).
8. Coetzee, C. J., Rohwer, E. F. C. H.: Cation exchange studies on ammonium-12-molybdophosphate. *J. Inorg. Nucl. Chem.* **32**, 1711 (1970).
9. Lin, M., Kajan, I., Schumann, D., Türler, A.: The concept for disposal of highly acidic spent nuclear fuel solutions at PSI. *J. Radioanal. Nucl. Chem.* **322**, 1857 (2019).
10. Available at: <https://www.lemerpax.com/en/products/clevasol-en/>. Accessed 10 July 2019.
11. Wells, A. F.: *Structural inorganic chemistry*. 2nd edition. Clarendon Press, Oxford, 351 (1950).
12. Van, J., Smit, R.: Ammonium salts of the heteropolyacids as cation exchangers. *Nature* **181**, 1530 (1958).
13. Buchwald, H., Thistlethwaite, W. P.: Some cation exchange properties of ammonium 12-molybdophosphate. *J. Inorg. Nucl. Chem.* **5**, 341 (1957).
14. Cannon, P.: A critical study of the precipitation of ammonium phospho-12-molybdate. *Talanta* **3**, 219 (1960).
15. Thistlethwaite, W. P., Watson, W. T.: The formation and composition of some metal 12-12-molybdophosphates. *J. Inorg. Nucl. Chem.* **24**, 1559 (1962).
16. Thistlethwaite, W. P., Watson, W. T.: The 12-molybdophosphates of Group II metals. *J. Inorg. Nucl. Chem.* **26**, 1815 (1964).
17. Thistlethwaite, W. P.: The “Normal” 12-molybdophosphates of the alkali metals and ammonium. *J. Inorg. Nucl. Chem.* **28**, 2143 (1966).
18. Dolezal, J., Stejskal, J., Tympl, M., Kourim, V.: Improved inorganic ion exchangers II. Ammonium molybdophosphate – silica gel system. *J. Radioanal. Nucl. Chem.* **21**, 381 (1974).
19. Rao, K. L. N., Mathew, C., Deshpande, R. S., Jadhav, A. V., Pande, B. M., Shukla, J. P.: Effects of electron beam irradiation on inorganic exchanger AMP. *Radiat. Phys. Chem.* **49**, 85 (1997).
20. Van, J., Smit, R.: Cation exchange properties of the ammonium heteropolyacid salts. *J. Inorg. Nucl. Chem.* **12**, 95 (1959).
21. Krtil, J.: Exchange properties of ammonium salts of 12-heteropolyacids-IV: Cs exchange on ammonium phosphotungstate and phosphomolybdate. *J. Inorg. Nucl. Chem.* **24**, 1139 (1962).
22. Chakravarty, R., Ram, R., Pillai, K. T., Pamale, Y., Kamat, R. V., Dash, A.: Ammonium molybdophosphate impregnated alumina microspheres as a new generation sorbent for chromatographic Cs-137/(Ba-137m) generator. *J. Chromatogr. A* **1220**, 82 (2012).
23. Murthy, G. S., Sivaiah, M. V., Kumar, S. S., Reddy, V. N., Krishna, R. M., Lakshminarayana, S.: Adsorption of cesium on a composite inorganic exchanger zirconium phosphate – ammonium molybdophosphate. *J. Radioanal. Nucl. Chem.* **260**, 109 (2004).
24. Sebesta, F., John, J., Motl, A., Stamberger, K.: Evaluation of polyacrylonitrile (PAN) as a binding polymer for absorbers used to treat liquid radioactive wastes. Contractor Report. Sandia National Laboratories. SAND95-2729 (1995).
25. Sebesta, F., John, J., Motl, A.: Phase II report on the evaluation of polyacrylonitrile (PAN) as a binding polymer for absorbers used to treat liquid wastes. Contractor Report. Sandia National Laboratories. SAND96-1088 (1996).
26. Ding, D., Zhang, Z., Chen, R., Cai, T.: Selective removal of cesium by ammonium molybdophosphate-polyacrylonitrile bead and membrane. *J. Hazard. Mater.* **324**, 753 (2017).
27. Pike, S. M., Buesseler, K. O., Breier, C. F., Dulaiova, H., Stastna, K., Sebesta, F.: Extraction of cesium in seawater off Japan using AMP-PAN resin and quantification via gamma spectrometry and inductively coupled mass spectrometry. *J. Radioanal. Nucl. Chem.* **296**, 369 (2013).

28. Park, Y., Lee, Y., Shin, W., Choi, S.: Removal of cobalt, strontium and cesium from radioactive laundry wastewater by ammonium molybdophosphate-polyacrylonitrile (AMP-PAN). *Chem. Eng. J.* **162**, 685 (2010).
29. Ingale, S. V., Ram, R., Sastry, P. U., Wagh, P. B., Kumar, R., Niranjana, R., Phapate, S. B., Tewari, R., Dash, A., Gupta, S. C.: Synthesis and characterization of ammonium molybdophosphate-silica nano-composite (AMP-SiO₂) as a prospective sorbent for the separation of ¹³⁷Cs from nuclear waste. *J. Radioanal. Nucl. Chem.* **301**, 409 (2014).
30. Deng, H., Li, Y., Huang, Y., Ma, X., Wu, L., Cheng, T.: An efficient composite ion exchanger of silica matrix impregnated with ammonium molybdophosphate for cesium uptake from aqueous solution. *Chem. Eng. J.* **286**, 25 (2016).
31. Wu, Y., Zhang, X., Wie, Y., Mimura, H.: Development of adsorption and solidification process for decontamination of Cs-contaminated radioactive water in Fukushima through silica-based AMP hybrid adsorbent. *Sep. Purif. Technol.* **181**, 76 (2017).
32. Samuelson, O.: Recommendation on ion exchange nomenclature. *Pure Appl. Chem.* **29**, 618 (1972).
33. Clifford, A. A.: Multivariate error analysis: a handbook of error propagation and calculation in many-parameter systems. John Wiley & Sons. ISBN 978-0470160558 (1973).
34. Todd, T. A., Mann, N. R., Tranter, T. J., Sebesta, F., John, J., Motl, A.: Cesium sorption from concentrated acidic tank wastes using ammonium molybdophosphate-polyacrylonitrile composite sorbents. *J. Radioanal. Nucl. Chem.* **254**, 47 (2002).
35. Rieman, W., Walton, H. F.: Ion-Exchange equilibrium. In: *Ion exchange in analytical chemistry*. Pergamon Press, Oxford, 36 (1970).
36. Suss, M., Pfrepper, G.: Investigation of the sorption of cesium from acid solutions by various inorganic sorbents. *Radiochim. Acta.* **29**, 33 (1981).
37. Ganzerli Valentini, M. T., Maxia, V., Rollier, M. A., Barbaro Forleo, M.: Behavior of Uranyl ion in nitric acid solutions with ammonium molybdophosphate. *J. Inorg. Nucl. Chem.* **32**, 671 (1970).
38. Krtil, J., Chavko, M.: Ion-exchange properties of ammonium salts of heteropolyacids. *J. Chromatogr. A.* **29**, 460 (1967).
39. Boyd, G. E., Adamson, A. W., Myers Jr, L. S.: The exchange adsorption of ions from aqueous solutions by organic zeolites. II. Kinetics. *J. Am. Chem. Soc.* **69**, 2849 (1947).
40. Kadous, A., Didi, M. A., Villemin, D.: A new sorbent for uranium extraction: ethylenediamino tris(methylenephosphonic) acid grafted on polystyrene resin. *J. Radioanal. Nucl. Chem.* **284**, 431 (2010).
41. Liu, H., Cai, X., Wang, Y., Chen, J.: Adsorption mechanism-based screening of cyclodextrin polymers for adsorption and separation of pesticides from water. *Water Res.* **45**, 3499 (2011).
42. Tranter, T. J., Herbst, R. H., Todd, T. A., Olson, A. L., Eldredge, H. B.: Evaluation of ammonium molybdophosphate-polyacrylonitrile (AMP-PAN) as a cesium selective sorbent for the removal of ¹³⁷Cs from acidic nuclear waste solutions. *Adv. Environ. Res.* **6**, 107 (2002).
43. Douglas LeVan, M., Carta, G., Yon, C. M.: Adsorption and Ion Exchange. In: *Perry's Chemical Engineer's Handbook*, 7th edition. McGraw-Hill, New York, 16-1 (1997).
44. Hameed, B. H., Din, A. T. M., Ahmad, A. L.: Adsorption of methylene blue onto bamboo-based activated carbon: kinetics and equilibrium studies. *J. Hazard. Mater.* **141**, 819 (2007).
45. Malik, P. K.: Dye removal from wastewater using activated carbon developed from sawdust: adsorption equilibrium and kinetics. *J. Hazard. Mater.* **113**, 81 (2004).
46. Sun, C., Sun, L., Sun, X.: Graphical evaluation of the favorability of adsorption processes by using conditional Langmuir constant. *Ind. Eng. Chem. Res.* **52**, 14251 (2013).
47. McKay, G., Blair, H. S., Gardner, J. R.: Adsorption of dyes on chitin. *J. Appl. Polym. Sci.* **27**, 3043 (1982).
48. Voudrias, E., Fytianos, K., Bozani, E.: Sorption-description isotherms of dyes from aqueous solutions and waste waters with different sorbent materials. *Global Nest J.* **4**, 75 (2002).
49. Goldberg, S.: Equations and models describing adsorption processes in soils. in: *Chemical processes in soils*. Soil Science Society of America, 677 S. Segoe Road, Madison, WI 53711, USA, 489 (2005).