

The Effect of Temperature on SuperLig<sup>®</sup> 644 Cesium Removal from  
Simulated Hanford Tank Waste Supernate (U)

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## ABSTRACT

Batch kinetic and column experiments have been carried out at 25, 35, and 45 °C to examine the effect of temperature on SuperLig<sup>®</sup> 644 cesium (Cs) removal from simulated Hanford tank waste supernate. The simulated solution mimicked the composition of the low-activity waste supernate from tank 241-AN-105 in the U.S. DOE Hanford site. Small quantities of toxic metals, such as Cd, Cr, Fe, and Pb were spiked into the simulant to evaluate the metal's competitiveness with Cs for sorption on SuperLig<sup>®</sup> 644 resin. The results indicated that the temperature affects the removal of Cs and metal ions, although the effect was not the same for all metal ions. The extent of Cs removal decreased with an increase in temperature. The Cs capacity at breakthrough point was 0.015, 0.013, and 0.011-mmole/g dry resin at 25, 35 and 45 °C, respectively. The column was effectively eluted to less than 1% (0.1 C/Co) of the feed concentration with approximately 10 BVs of 0.5 M nitric acid. The resin showed limited affinity for Fe and toxic metal ions (Cr, Cd, and Pb) as compared to Cs. Based on the batch kinetic data, the Cs uptake of the resin was not hampered by the presence of the Fe or toxic metals in solution.

## Introduction

The River Protection Project Waste Treatment Plant (RPP-WTP) at the Hanford site has identified a process to pre-treat and vitrify Hanford tank waste supernatants into a low activity and high level waste glass. The process for treatment of Hanford waste removes  $^{137}\text{Cs}$ ,  $^{99}\text{Tc}$  (as pertechnetate ion,  $\text{TcO}_4^-$ ), and  $^{90}\text{Sr}$  and transuranic isotopes. The pretreatment unit operations of the RPP-WTP process are sludge washing, filtration, precipitation, and ion exchange. Each process unit removes some radionuclides from the bulk of the waste and concentrates them into a small-volume of high level waste (HLW) mixture. This mixture is vitrified as high activity glass. The decontaminated aqueous Low Activity Waste (LAW) phase contains the bulk of the waste volume and is vitrified as a low activity glass.

The  $^{137}\text{Cs}$  removal is accomplished using SuperLig<sup>®</sup> 644 (Trademark of IBC Advanced Technologies, American Fork, Utah). This resin has been selected as the baseline ion exchange material for Cs removal from Hanford tank waste solutions. The elutable resin contains covalently bound macrocyclic ligands that have high affinity for Cs ion in alkaline solution in the presence of sodium and potassium. Extensive experimental investigations conducted at the Savannah River Technology Center (Aiken, South Carolina) and Battelle Pacific Northwest National Laboratory (Hanford, Washington) with simulated Hanford tank waste solutions indicated that SuperLig<sup>®</sup> 644 resin has adequate density and low-cycle physical durability<sup>1</sup>, sufficient chemical stability<sup>2</sup>, sufficient Cs sorption capacity and selectivity<sup>3</sup>. Radioactive Hanford Site tank waste samples from tanks 241-AN-103, 241-AN-102, and 241-AZ-102 confirmed the

simulant results.<sup>5,6</sup> All the experimental investigations performed to date were at ambient temperature and the effects of solution temperature have not been sufficiently assessed to understand the impact of temperature on the resin performance. Since the seasonal temperatures can vary widely, a possible equilibrium shift caused by elevated summer temperatures could severely impact the performance and durability of the SuperLig<sup>®</sup> 644 resin. Toxic metal ions were also excluded from the previous simulated waste solutions due to the assumption that SuperLig<sup>®</sup> 644 is sufficiently selective against sodium and potassium with minimal co-sorption potential of minor toxic chemicals.

In this study, batch kinetic and small column experiments were performed with simulated Hanford tank waste supernate. The batch kinetic experiments were performed to determine the distribution coefficients ( $K_d$  values) for Cs and metal ions, Cd, Cr, Fe, and Pb as a function of time and different temperatures. The column tests were performed at 25, 35 and 45 °C to examine the impact of operational temperature on the column loading and elution performance.

## Experimental

### Simulated Hanford Waste Solution

Because of the limited availability and the experimental cost associated with using radioactive waste samples, testing with simulated waste solutions is imperative to assess process performance with a mock experimentation. In this work, simulated Hanford tank waste solution, which mimics the composition of U. S. DOE Hanford site tank 241-AN-105 was used. A five-liter batch of the simulant at approximately 5.0M Na<sup>+</sup> concentration was prepared using the best available analytical characterization data.<sup>7</sup> The simulant was spiked with metals Cr, Cd, Pb, and Fe, then allowed to stand for 24 h before filtering through a 0.45- $\mu$ m filter. Duplicate samples of the simulant were analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) to determine the concentrations of the metal constituents. The Cs was replenished with cesium nitrate after the simulant preparation was completed and the concentration was determined by inductively coupled plasma mass spectroscopy (ICP-MS). The chemical composition of the simulated waste solution is given in Table 1.

### Ion Exchange Resin

The SuperLig<sup>®</sup> 644 resin (batch # 991022SMC-IV29) was used for the batch kinetic and column experiments. IBC Advanced Technologies, American Fort, Utah, supplied the resin. The resin was received in potassium form as 20-70 mesh granules. It was desirable to remove the impurities that have been left from the resin manufacturing process and to convert the resin into hydrogen form prior to the Cs ion exchange tests.

For this purpose, samples of the “as received” resin in the potassium form were treated with dilute nitric acid (0.5 M) and sodium hydroxide (1 M) solutions. Approximately 50 g ( $\pm 0.01$  g) of the resin (batch # 991022SMC-IV29) was weighed in a high density polyethylene (HDPE) bottle and soaked in 1.0 M sodium hydroxide solution for 2 hrs. The solution to resin phase ratio was taken as 10:1 (i.e. mL solution/g dry resin). The resin and sodium hydroxide solution mixture was gently shaken several times, but no magnetic bar or mechanical stirrer was used. The resin was slurried into a glass column of 2.7 cm in diameter and 35 cm in height. After discarding excess sodium hydroxide solution from the column, the resin was washed with 3 bed volumes (BVs) of deionized water, followed by 15 BVs of 0.5 M nitric acid. The resin was again washed with 10 BVs of deionized water, then removed from the column and oven dried at 50 °C in a vacuum oven at 24 in Hg. The dry resin (~ 20 g) was stored in a sealed screw-capped bottle to ensure it was not exposed to an oxygen environment prior to the experiments.

Scanning electron microphotographs (SEM) and X-ray diffraction (XRD) of the original and pretreated resin samples were taken. Comparison of the SEM and XRD patterns of the original and pretreated samples show that the two samples had the same porous structure, and rough surfaces and the morphology of the resin samples was basically the same. The original potassium form samples of the resin were analyzed by wet chemical method and it was determined that the form contained ~ 60 %  $\text{KCO}_3$ . Some important physical properties of the resin samples such as the apparent density, particle size distribution, true density, and moisture content were measured and presented in Table 2.

Apparatus:

The equipment used for batch contact tests consisted of a benchtop incubator shaker (model C24) supplied by New Brunswick Scientific Co., Edison New Jersey; Nalgene<sup>®</sup> filter units supplied by Nalgene Nunc International, Rochester, New York; and an analytical balance, (model AG285) obtained from Mettler Toledo. The analytical balance was accurate to  $\pm 0.001$  g. A high precision (0.01 °C) thermometer traceable to NIST calibration was mounted in polyethylene bottles containing de-ionized water to record the temperature in the incubator shaker environment. A house-supplied vacuum and a trap assembly were used during sample filtration. All experiments were performed in a chemical hood.

The equipment for ion exchange column tests included a single column, a positive displacement pump, an automatic fraction collector, and a water circulator. The column was constructed from borosilicate glass tubing with 1.45-cm i.d., and a total length of 30 cm. The outside of the column walls was coated with a layer of clear polyvinylchloride to reduce hazards associated with potentially pressurizing the apparatus. The column top assemblies had a fill reservoir, a pressure gauge, a pressure relief valve, and a feed inlet port. The fill reservoir on column top assemblies also served as a vent. The top assembly was connected to the lower section by a glass ground joint and was tightly fitted by a screw cap. A ruler affixed to the column wall was used to allow observation of resin bed height and liquid level changes. All tubing connections were made of polypropylene lines that had Teflon<sup>®</sup> quick-connect fittings attached to each end. A 3-way, 6 mm bore Teflon<sup>®</sup> stopcock (#1) was attached to the bottom of the column. The column head was attached to the column using a Rudivis ground-glass

joint. Two 2-way, 6 mm bore stopcocks (#2 and #3) were attached on opposite sides of the column head to serve as feed ports. The column head also contained a pressure gauge, a pressure relief valve, and a fill reservoir that also served as a vent. Stainless steel wire screens (200 mesh) were inserted into the columns to support the ion exchange resin. Quick-disconnect couplings supplied by Colder Products Company, St. Paul, Minnesota, were used to connect low-density polyethylene tubing (11/64" i.d.) to the column. All solutions were passed as down flow through the column using a Fluid Metering Incorporated (FMI) positive displacement pump. Scilog, Inc., Middletown, Wisconsin, supplied the pump head (model RH00). It was made of a stainless steel (1/8" i.d.) piston that is rotated by a 450 rpm optically encoded, servo-controlled motor. The flow rate range for the pump head/piston configuration was 0-23 mL/min. Samples were collected either manually or using a Spectrum Chromatography IS-95 Interval Sampler.

## Procedure

### Batch Contact Experiments

In order to obtain the distribution coefficients ( $K_{ds}$ ) for Cs and toxic metal ions, batch kinetic experiments were carried out at different temperatures. In all tests, the resin-to-solution phase ratio was 1:100 g/cm<sup>3</sup>. The initial concentrations of Cs, Cr, Cd, Fe, and Pb were 7.25, 592, 0.4, 0.77, and 21.5 mg/L, respectively. All measurements were carried out in duplicate. A known volume (~18 ml) of the simulated Hanford tank waste solution was contacted with a known quantity (~0.18 g) of pretreated hydrogen form resin in screw-cap polyethylene bottles. The batch contact tests were carried out at 25, 35, and 45 °C. The bottles containing the solution and the resin were placed in an incubator- shaker.

The shaking speed of the incubator was set at 275 rpm, and the temperature was set to the desired level (i.e., 25, 35, or 45 °C) and continuously monitored by placing de-ionized water bottles mounted with high precision thermocouples in a location adjacent to the simulant test bottles. The tests were all conducted in duplicate for  $72 \pm 1$  hr. Blank control samples (~ i.e., 18 mL of the simulated waste solution) containing no ion exchange resin were processed in identical steps as the simulated waste samples. The concentrations of Cs and competing metal cations in the blank samples were used as initial concentrations for the determination of distribution coefficients ( $K_{ds}$ ). Sub-samples of the simulant in contact with the resin were removed from the solution using individual 0.45-micron filter syringes at time intervals of 1, 4, 8, 24, 48, and 72-hours. The samples were analyzed by ICP-MS to determine the concentration of total Cs and by ICP-AES to determine the concentrations of sodium, potassium, and toxic metal competitors, such as cadmium, chromium, iron, lead, and calcium. The amounts of simulant solution withdrawn at each interval were higher than wanted, and this resulted in a gradual change of the phase ratio. Conducting a material balance on each sample mitigated the effect of this procedural err on the results and the details are discussed later.

The amount of test solution withdrawn at each interval (~ 1 mL) was higher than wanted and presumably the final solution weight differed slightly from that of the pre-withdrawal test solution. We made appropriate final corrections to account for the fact that the liquid-to-solid ratio and the remaining concentrations of the species decreased as successive assay portions were withdrawn. To determine the  $K_{ds}$  of sorbed species, we compared the concentration of the species in the post-assay solution with the

concentrations in the pre-assay solution and corrected for the amount and concentration of each species in the assay removed.

### Small-Scale Column Tests

A known mass (2.25 g) of pretreated SuperLig<sup>®</sup> 644 (batch # 991022SMC-IV29) resin was slurried into a 1.45 cm (~0.6-inch) i.d. glass column using de-ionized water. The outside walls of the column were tapped while the resin was being slurried into column to ensure uniform packing of the resin bed. The initial height of the resin bed in de-ionized was approximately 3.0-cm (~1.2-inches), yielding a column that contains ~5 mL of resin in the hydrogen form. The temperature of the water-bath circulator and the column jacket were adjusted at 25 °C. The temperature of the liquid above the resin bed was periodically measured and recorded during the tests. Six bed volumes (BVs) of 0.25M sodium hydroxide solution was pumped as downflow into the column at approximately 1 bed volume per hour (BV/h). The resin was stored overnight in the sodium hydroxide solution to allow for maximum swelling of the resin. After overnight storage, the NaOH liquid level was adjusted so the volume of liquid above the resin bed was approximately 2 cm. The height of the resin bed was approximately 8 cm (3.1 inches), yielding a column that contained ~ 13-mL of swollen resin in sodium form. The preconditioning solution (0.25M NaOH) that remained above the resin bed and in the feed tubing was approximately 1 BV; the total apparatus volume (TAV) was equal to 2 BV. Therefore, the first 11.2-mL of simulant that was fed into the column at the beginning of the loading cycle was diluted by a factor of 2. Likewise, the post-feed water wash and the eluting solutions were allowed to mix with the liquid head left above the

resin from the previous cycle. No attempt was made to correct for mixing of solutions in the column headspace when calculating the number of bed volumes of feed, wash, or eluate processed.

Loading of the resin bed at the desired temperature was considered to start at the moment that the simulant contacted the resin bed. The simulant was pumped as downflow through the column at  $\sim 3$  BV/h. The first 3 BV of effluent was discarded to prevent dilution of the effluent by residual sodium hydroxide solution. Sub-samples of the column effluent were collected after 5 BV of solution had passed through the column and at intervals of approximately 10 BVs, until approximately 150-BVs of simulant had been processed. The samples were collected using a Spectrum Chromatography IS-95 Interval Sampler. Periodically (during sample collection, except off shift hours), the heights of the resin bed and the liquid above, the temperatures of the water-bath circulator and the resin bed, and the flow rate were measured and recorded. The column effluent samples were analyzed to determine the concentrations of Cs by ICP-MS and metal ions by ICP-AES.

At the conclusion of the loading cycle, the simulant was displaced from the column using 6 BVs (2 total apparatus volumes) of 0.1M sodium hydroxide solution. The dilute sodium hydroxide solution was pumped as downflow into the column at 3 BV/hr. The resin bed was then flushed with 6 BVs of de-ionized water at the same flow rate (3 BV/h). The dilute sodium hydroxide was used in order to prevent aluminum hydroxide precipitation that could foul the resin bed, and the water rinse served to displace residual sodium hydroxide solution from the columns prior to elution. The column was eluted

using 16 BV of 0.5 M nitric acid solution at 1.4 BV/hr. Sub-samples of the column eluate were collected in 2-BV increments and were analyzed for total Cs by ICP-MS; composite elute solution was analyzed for total Cs (ICP-MS) and the metal constituents by ICP-AES. Upon conclusion of the elution cycle, the residual nitric acid solution was displaced from the column by pumping 6 BVs of de-ionized water through the column at 1 BV/hr. The column was stored in the de-ionized water for 2 days before the column tests were initiated. The column tests at elevated temperatures (35 and 45 °C) were carried out using fresh simulant. The polypropylene tubing (feed line), the resin bed and the solution bottles containing the feed, regenerant (0.25 M NaOH), displacement (0.1 M NaOH), deionized water, and the eluant (0.5 M HNO<sub>3</sub>) were preheated to the desired elevated temperature.

## Results and Discussion

### Batch Kinetic Results

Temperature is an important factor controlling the selectivity of ion exchange resins. The distribution coefficient ( $K_d$ ) characterizes the selectivity of the resin for metal ions. The  $K_d$  is represented by the ratio of metal ion concentration on the resin to the metal concentration in solution and it can be calculated using the following equation:

$$K_d = \left[ \left( \frac{C_{init}}{C_{final}} \right) - 1 \right] \left[ \frac{V}{M * F} \right] \quad (1)$$

where  $C_{\text{init}}$  and  $C_{\text{final}}$  are the metal ion concentrations in the solution before and after contacting with resin,  $V$  is the volume of solution used,  $M$  is the mass of the dry resin, and  $F$  is the ratio of wet to dry weight of the resin (correction factor). The distribution coefficients are typically measured at equilibrium so the data represents one point on the equilibrium isotherm. The distribution coefficients determined at various contact times before attaining equilibrium were generally termed as the “time-dependent”  $K_d$  values and they describe the kinetic behavior of the resin during the ion exchange process.

Figs. 1-5 show the  $K_d$  values for Cs, Cr, Cd, Fe, and Pb as a function of time and different temperatures. In Fig. 1, the Cs  $K_d$  increased with contact time until equilibrium was established in about 48 h. The temperature effect on the  $K_d$  was negligible for contact times less than 24 h; this is significant in the operation of full-scale ion exchange columns where a normal residence time of less than 2 hours is expected. At contact times beyond 48 h, the Cs  $K_d$  slightly decreased with increasing temperature. A previous study by Bray et. al., showed that selectivity for Cs tends to decrease as the temperature is increased for most ion exchangers.<sup>8</sup> The very large Cs  $K_d$  values observed for all temperatures would explain that the Cs selectivity of the resin was not hampered by presence of toxic metal ions. Fig. 2 shows the time-dependent  $K_d$  of Cr at 25, 35, and 45 °C. The results indicate that equilibrium was established in about 24 h and the Cr  $K_d$  value decreased with the contact time beyond 24 h. The Cr  $K_d$  increased with an increase in temperature. The very low  $K_d$  values for Cr (averaging between 10 and 40 mL/g)

would indicate that the SuperLig<sup>®</sup> 644 has little affinity for Cr sorption from the simulant solution.

Figs. 3 and 4 show the results of Cd and Fe sorption on SuperLig<sup>®</sup> 644 resin as a function of contact time at 25, 35, and 45 °C, respectively. In the lower temperature range (25-35 °C), the time-dependent  $K_d$  of Fe slightly decreased with an increase in temperature, but the influence of the temperature on the Cd  $K_d$  was negligible in this temperature range. At 45 °C, the  $K_d$ s for both Fe and Cd increased dramatically with contact time beyond 24 h. The reason for the dramatic  $K_d$  increases is not known at this stage. Fig. 5 shows the results of Pb  $K_d$  a function of contact time and temperature. It can be seen that equilibrium was established for Pb in about 48 h, but the  $K_d$  slightly dropped thereafter. The time-dependent  $K_d$  values measured for Pb at 25, 35, and 45 °C were within experimental errors of each other and, therefore, no clear influence of the temperature was noted under the experimental condition tested.

#### Column Loading Results

The effect of temperature on ion exchange column loading is rather a complex function of the material's total ion exchange capacity and selectivity, mass transfer and diffusion, and resin density and swelling characteristics. Lower temperatures generally favor column loading, but the loading rate will be lower since the diffusion rate is expected to diminish with temperature. Conversely, higher temperatures would increase the diffusion rate and solubility of waste solution components, but again the capacity will decrease. The density of the ion exchange material regulates the quantity of metal ion that

can be removed from waste solution at specified solution temperature and flow rate. Therefore, it is important to assess the behavior of the ion exchange material in a flowing system and to define the optimum processing conditions.

Table 3 shows a summary of the results for Cs loading on the SuperLig<sup>®</sup> 644 resin at different temperatures. The estimated bed volumes to reach 50% breakthrough (0.5 C/Co) were approximately 170, 150, and 125 for the solution temperatures 25, 35, and 45 °C. The loading of the column at different solution temperatures was carried out at ~ 3 BV/h (0.98 cm/min) using the same resin bed for all tests. The column loading was repeated for a second time at 25 °C after the resin exposure to the elevated temperatures (35 and 45 °C). Approximately 50% breakthrough was achieved at 165 BVs for the repeat test. A summary of the swelling and shrinking history of the resin bed during the column loading at different temperatures is presented in Table 4. The average volumes of the resin bed during regeneration, loading, and elution were 13.7, 11.1, and 7.6 ml, respectively. The extent of swelling that the resin bed undergoes from a load solution to elution was calculated from the height changes, using the following equation:

$$\% \text{ swelling} = \left| \frac{(\rho_{bed} \text{ in sol'n} - \rho_{bed} \text{ in acid})}{\rho_{bed} \text{ in sol'n}} \right| \times 100 \quad (2)$$

where  $\rho_{bed}$  in sol'n represents the bed density in respective (load or regenerate) solutions and  $\rho_{bed}$  in acid represents the eluted bed density. For SuperLig<sup>®</sup> 644, the bed density decreased from an average of about 0.296 g/mL in 0.5 M HNO<sub>3</sub> to about 0.165 g/mL in regenerate (0.25 M NaOH) solution. This was equivalent to about 80% swelling of the

resin bed. The difference in the bed densities in load (simulant) and elution (0.5 M HNO<sub>3</sub>) solutions was equivalent to about 45% swelling. It was noted that the resin bed contracted about 19% (vol.) during the column loading with simulated waste solution. The resin contraction was due to exchange of large hydrated Na ions on the resin with much smaller hydrated Cs ions from the feed solution. When the exchange of Na with Cs occurs, the resin is able to contract. Swelling is desirable for the resin to undergo ion exchange with Cs and metal ions. In addition, swollen resin allows for faster mass transfer by reducing intraparticle resistance. The resin swelling, however, can become undesirable from an operations point of view since swelling could potentially cause channeling. The swelling and shrinkage behavior of the resin was invariant with temperature under the present experimental conditions.

Fig. 6 shows the Cs breakthrough curves at 25, 35, and 45 °C. The plots show the concentration of Cs in the effluent divided by the initial concentration in the feed as a function of the number of bed volumes of simulant processed at initial Cs concentration in the feed of 7.25 mg/L. The Cs loading decreased with an increase in solution temperature (i.e., the Cs breakthrough curve was shifted upward towards less volume) was increased from 25 to 45 °C. At 45 °C, 70% Cs breakthrough was observed after 150 BVs as compared to only 41% Cs breakthrough at 25 °C. The capacity of the resin at breakthrough point (defined as the amount of Cs that loaded per unit mass of resin in the column before being detected in the outlet of the column) was 0.015, 0.013, and 0.011-mmole/g dry resin at 25, 35 and 45 °C, respectively. The shape of the Cs breakthrough curves at different temperatures was sigmoidal with remarkable similarity to each other.

Fig. 7 shows the Cs elution results at different solution temperatures. The elution was performed using 0.5 M nitric acid solution at ~1 to 1.4 BV/h. The Cs elution data are plotted in semi-log probability form where the Cs concentration is normalized to the initial feed concentration. It can be seen that the curves display characteristic elution behavior. At the front end of the curves, the Cs concentration profile ( $C/C_0$ ) was low because of the dilution from the caustic (0.1 M NaOH) wash and water rinse solutions that followed the loading phase. As these solutions were replaced by the flow of 0.5 M HNO<sub>3</sub> into the column, the pH was reduced as well as the Cs distribution coefficient and the Cs elution started to elute immediately from the column. The Cs peak concentration for all three temperatures was reached after approximately 4 to 6 BV of 0.5 M HNO<sub>3</sub> was transferred into the column. An exponential decline of the Cs concentration was then observed after the elution peak. The Cs on the column was exhausted to less than 1% of the feed concentration (0.1  $C/C_0$ ) in approximately 14 BVs. The influence of temperature on the Cs elution was not significant under present experimental conditions.

The toxic metal ions were analyzed along with Cs for possible breakthrough behavior. Figs. 8-11 show the breakthrough curves of Cd, Cr, Fe, and Pb at different solution temperatures. It should be noted that none of these metal ions exhibited a breakthrough curve similar to that of the Cs. The shape of Cd and Fe breakthrough curves changed from a gradual increase of the concentration profile in the temperature range 25-35 °C to a steep rise of the concentration profile to a plateau at 45 °C. The temperature influence on Cd and Fe loading on SuperLig<sup>®</sup> 644 was similar to the Cs in the initial stages of loading. However, the concentration profiles of Cd and Fe at 35 °C dramatically

increased after 60 BV and essentially exceeded the feed concentrations (Figs. 8 and 10), suggesting metal ion leakage from the resin. Such metal ion leakage could result from metals accumulation during the prior column loading 25 °C and retention during the elution phase. Elution after the first column loading (at 25 °C) was carried out at a flowrate higher than desired (1.4 BV/h vs. 1 BV/h) and the Cd and Fe elution peaks were insignificant, indicating that these species were not completely eluted from the resin.

Figs. 9 and 11 show the breakthrough curves for Cr and Pb at 25, 35, and 45 °C. It can be seen that the Cr breakthrough from the column was instantaneous. The first two data points on the breakthrough curve were low because of the dilution of the effluent samples by approximately one bed volume of 0.25 M NaOH left over from the regeneration step. Beginning with the third data point, the concentration of Cr essentially reached the feed concentration. The breakthrough of Pb was immediately observed as indicated by the steep rise of concentration profiles to a near maximum value of  $\sim 1.0 C/Co$  (Fig. 11). The early breakthrough results could result from poor diffusion-controlled column kinetics. The temperature influence on the loading behavior for Cr and Pb was not obvious since there was a wide variability in the analytical data.

The elution behavior of the metal ions was shown in Figs. 12 to 15. Elution was accomplished using 0.5 M nitric acid solution at approximately 1 BV/h; except the elution of the first column loading (at 25 °C) was performed at 1.4 BV/h. Fig. 12 shows the Cd elution profiles at 25, 35 and 45 °C. The peak concentration of Cd was 20 times higher than the feed concentration, indicating that the resin concentrated Cd ions during the loading phase. The Cd concentration on the resin after passing at 16 BVs of eluant

through the column was less than 10% of the feed concentration ( i.e., 0.1 C/Co). Fig. 13 shows the Cr elution from the column at different temperatures. Since Cr was significantly loaded onto the column, the peak concentration was expectedly low ( $< 0.5$  C/Co). The elution tail indicated that trace Cr was picked up by the resin during the loading phase even though the effect was not visible from the breakthrough data.

Elution curves of Fe and Pb are displayed in Figs. 14 and 15, respectively. The Fe elution profile increased from a below 0.1 C/Co to a peak concentration of 20 times the feed concentration. A significant elution tail was observed for Fe. Retention of Fe by the resin is of major concern because it could interfere with subsequent loading cycles by contributing to the loss of resin capacity through chemical degradation or fouling. Fig. 20 shows the Pb elution profile at 25, 35, and 45 °C. The Pb elution profile increased from less than 3% of the feed concentration (0.03 C/Co) to a peak elution of 4 times the feed concentration. The concentration profile at exhaustion (at 16 BVs) was  $< 0.1$  C/Co.

## Conclusion

Batch kinetic and column-loading experiments were performed to evaluate the effects of temperature on Cs sorption on SuperLig<sup>®</sup> 644 resin. The Cs distribution coefficients were obtained as a function of contact time at 25, 35, and 45 °C. Loading and elution profiles were also obtained for Cs and several trace metal ions in the simulated Hanford tank waste solution at these temperatures. The rate of resin degradation in various storage solutions was examined at 45 °C. The results from column

tests showed that more than 100 BVs of the simulated Hanford waste tank (Tank 241-AN-105) feed were processed for the temperatures 25 °C, 35 °C and 45 °C before 50% breakthrough of the Cs occurred. The Cs loading on the resin columns decreased as the temperature was increased. Cs elution from SuperLig® 644 resin was complete after passing 15 BVs of 0.5 M nitric acid into the columns. The effect of temperature on the elution was insignificant under present experimental conditions. Trace metals (cadmium, chromium, iron, and lead) spiked into simulated Hanford waste solution were adsorbed onto SuperLig® 644 resin. The uptake of the metal ions increased in the sequence Fe >Cd >Pb >Cr. These metals were often omitted from simulant solutions due to the assumption that SuperLig® 644 was sufficiently selective for Cs and minimal co-sorption potential existed for these metal ions.

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## References

1. Brown, G. N., Bray, L. and Elovich, R. J., "Evaluation and Comparison of SuperLig® 644, Resorcinol-Formaldehyde and Cs-100 Ion Exchange Materials for the removal of Cs from Simulated Alkaline Supernate," PNL-10486, Pacific Northwest Laboratory, Richland, WA, March, 1995.
2. Brown, G. N., Adami, S. R., Bray, L. A., Bryan, S. A., Carlson, C. D., Carson, K. J., Deschane, J. R., Elovich, R. J., Forbes, S. J., Franz, J. A., Linehan, J. C., Shaw, W. J., Tanaka, P. K. and Telander, M. R., "Chemical and Radiological Stability of SuperLig® 644, Resorcinol-Formaldehyde and Cs-100 Cesium Ion Exchange Materials," PNL-10722, Pacific Northwest Laboratory, Richland, WA, September, 1995.
3. Brown, G. N., Bray, L.A., Carlson, C. D., Carson, K. J., Deschane, J. R., Elovich, R. J., Hoopes, V. F., Kurath, D. E., Nenninger, L. L. and Tanaka, P. K., "Comparison of organic and inorganic Ion Exchangers for Removal of Cesium and Strontium from Simulated and Actual Hanford 241-AW-101 DSSF Tank Waste," PNL-10920, Pacific Northwest National Laboratory, 1996.
4. Hassan, N. M., McCabe, D. J, King W. D., Hamm, L. L., and Johnson, M. E., "Small-Scale Ion Exchange Removal of Cesium and Technetium from Hanford Tank 241-AN-103," BNF-003-98-0146, Rev.1, Westinghouse Savannah River Company, August, 1999.
5. Hassan, N. M, McCabe, D. J., King, W. D. and Hamm, L. L., Johnson M. E., "Ion exchange removal of cesium from Hanford tank waste supernates with SuperLig® 644 resin," J. Radioanal. Nucl. Chem. 2002, 254 (1), 33-40.
6. Hassan, N. M, McCabe, D. J., King, W. D. and Hamm, L. L., Johnson M. E "SuperLig® 644 equilibrium sorption data for cesium from Hanford tank waste supernates," J. Radioanal. Nucl. Chem. 2002, 253 (3), 361-367.

7. Eibling, R.E., Nash, C.A., “Hanford Waste Simulants Created to Support the Research and Development on the River Protection Project – Waste Treatment Plant,” WSRC-TR-2000-00338, SRT-RPP-2000-00017, Westinghouse Savannah River Company, March, 2001.
8. Bray, L. A., Carson, K. J., Kovich, R. J., Kurath, D. E., “Equilibration Data for Cesium Ion Exchange of Hanford CC and NCAW Tank Waste,” TWRSP-92-020, Pacific Northwest Laboratory, Richland, WA, September, 1992.
9. Kurath, D. E., Bray, L. A., Brooks, K. P., Brown, G. N., Bryan, S. A., Carlson, C. D., Carson, K. J., DesChane, J. R., Elovich, R. J., Kim, Y. A., “Experimental Data and Analysis to Support the Design of an Ion Exchange Process for the Treatment of Hanford Tank Waste Supernate Liquids,” PNL-10187, Pacific Northwest National Laboratory, Richland, WA, December 1994.
10. Kunin, R. Ion Exchange resins, John Wiley & Sons, Inc. New York, 153.

Table 1. Simulant composition (tank 241-AN-105)

Analyte	avg. (mg/L)
Cs, mg/L	7.25E+00
Total carbon, mg/L	
TIC, mg/L	3.26E+03
TOC, mg/L	1.20E+03
Free OH, M	8.44E-01
Total hydroxide ( M)	2.29E+00
Specific gravity	1.23E+00
ICP-ES, mg/L	
Al	1.58E+04
B	2.35E+01
Ba	5.44E-01
Ca	2.99E+00
Cd	3.99E-01
Cr	5.92E+02
Cu	<1.0E-01
Fe	7.75E-01
Mo	3.62E+01
Na	1.14E+05
Ni	9.72E-01
P	7.17E+01
Pb	2.15E+01
Si	1.42E+02
Sr	1.20E-01
Zn	4.87E+00
K	3.43E+03
Na/Cs	1.57E+04
K/Cs	4.73E+02

**Table 2. Physical property of SuperLig<sup>®</sup> 644**

U. S mesh	mesh opening	weight of fraction (g)		wt. % (normalized)		ave. wt. % (%)
		Sample # 1	Sample # 2	Sample # 1	Sample # 2	
<b>30</b>	<b>&gt; 600</b>	<b>3.1794</b>	<b>3.4253</b>	<b>66.15</b>	<b>69.36</b>	<b>67.76</b>
<b>40</b>	<b>&gt; 425</b>	<b>0.9969</b>	<b>1.067</b>	<b>20.74</b>	<b>21.61</b>	<b>21.17</b>
<b>50</b>	<b>&gt; 300</b>	<b>0.4064</b>	<b>0.31</b>	<b>8.46</b>	<b>6.28</b>	<b>7.37</b>
<b>50-70</b>	<b>&gt; 212</b>	<b>0.2038</b>	<b>0.1228</b>	<b>4.24</b>	<b>2.49</b>	<b>3.36</b>
<b>70-80</b>	<b>&gt; 180</b>	<b>0.0138</b>	<b>0.0086</b>	<b>0.29</b>	<b>0.17</b>	<b>0.23</b>
<b>80-100</b>	<b>&gt; 150</b>	<b>0.0028</b>	<b>0.002</b>	<b>0.06</b>	<b>0.04</b>	<b>0.05</b>
<b>230</b>	<b>&gt; 62</b>	<b>0.0032</b>	<b>0.0025</b>	<b>0.07</b>	<b>0.05</b>	<b>0.06</b>

Table 3. Summary of Column Test Results

Test #	Temperature (°C)	Resin bed* volume (mL)	Flow rate (BV/h)		Total # BV processed	# BV @ 50% bkth
			Loading	Elution		
1	25	11	3	1.4	140	170 **
2	35	11	3	1	140	150 **
3	45	11	3	1	150	125
4	25	11	3	1	210	165

\* mass of resin in the column= 2.25 g

\*\* Projected to 50% breakthrough

Table 4. Resin Bed Swelling and Shrinking History (values in mL)

Test #	Temperature (°C)	0.25M NaOH	5M Na+ simulant	0.1M NaOH	0.5M HNO <sub>3</sub>
1	25	13.2	11.2	13.7	8.1
2	35	14.1	11.2	13.2	7.6
3	45	13.7	10.9	12.7	7.1
4	25	12.9	10.9	13.2	7.4

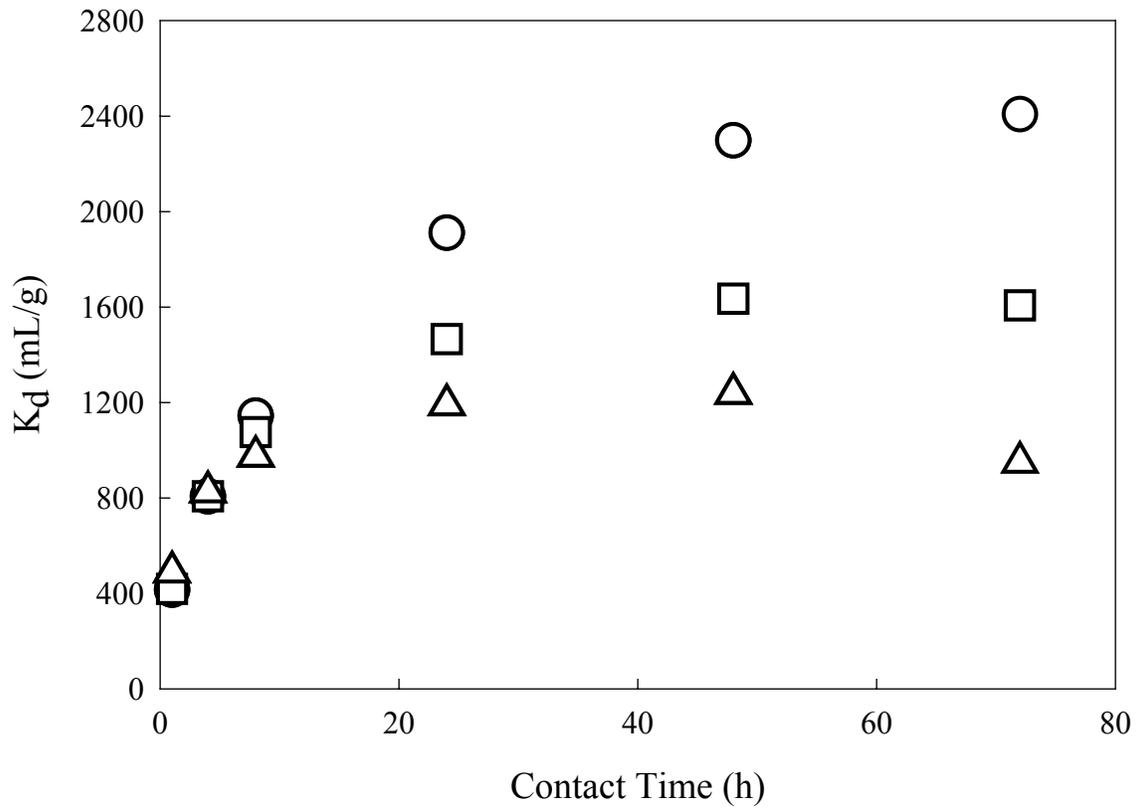


Fig. 1. Temperature effect on cesium  $K_d$  as a function of time

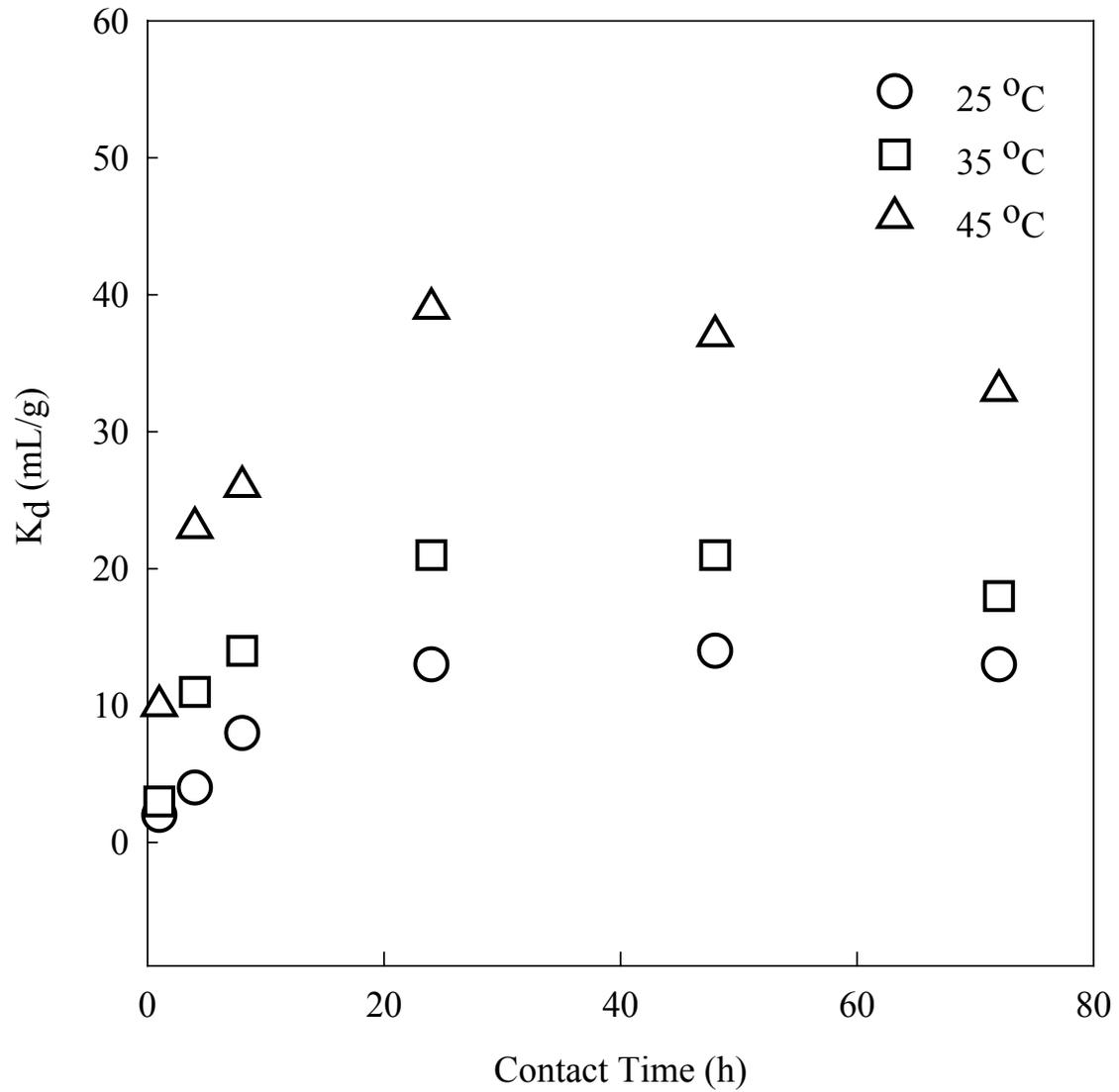


Fig. 2. Temperature effect on Cr K<sub>d</sub> as a function of time

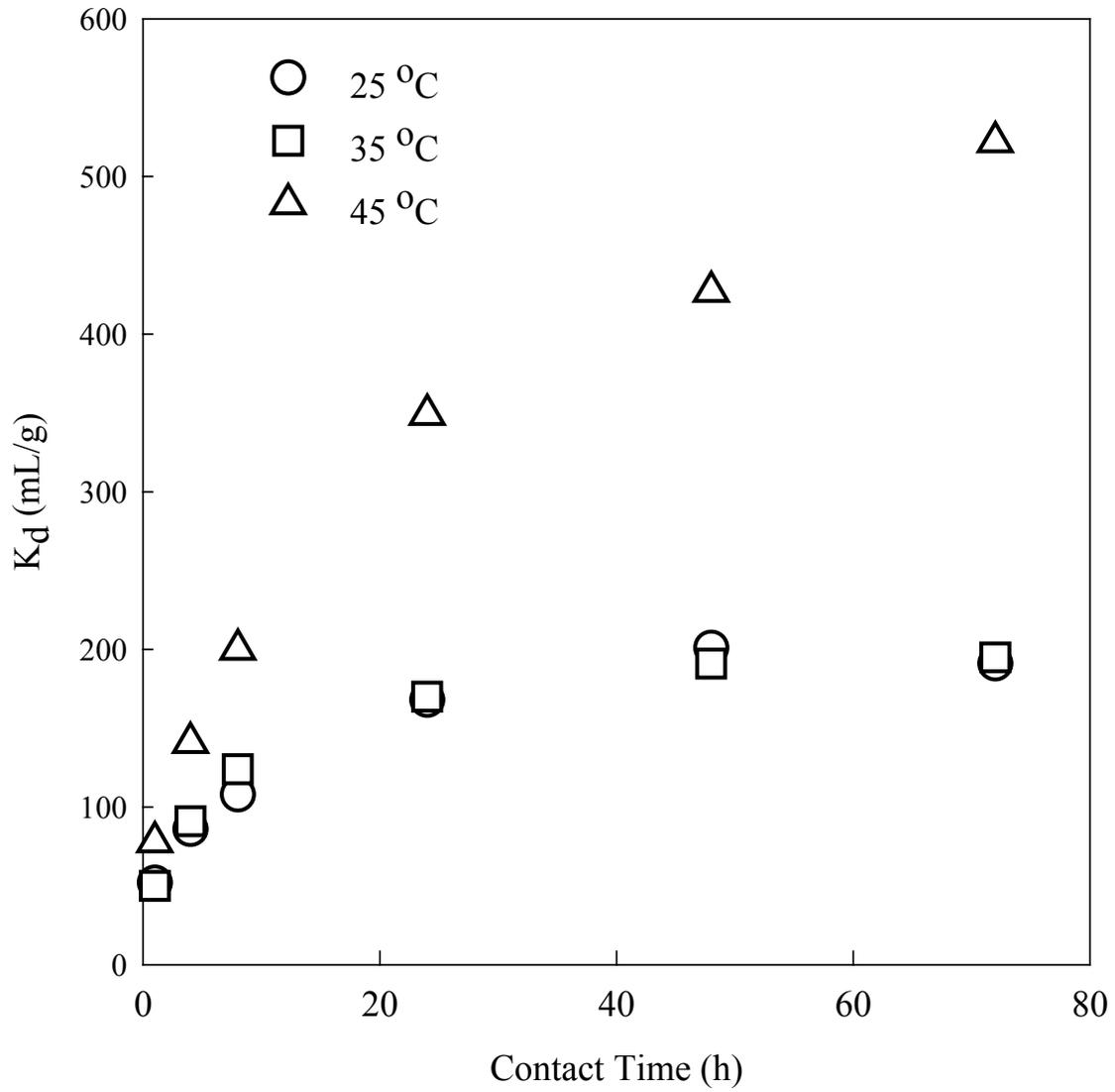


Fig. 3. Temperature effect on cadmium  $K_d$  as a function of time

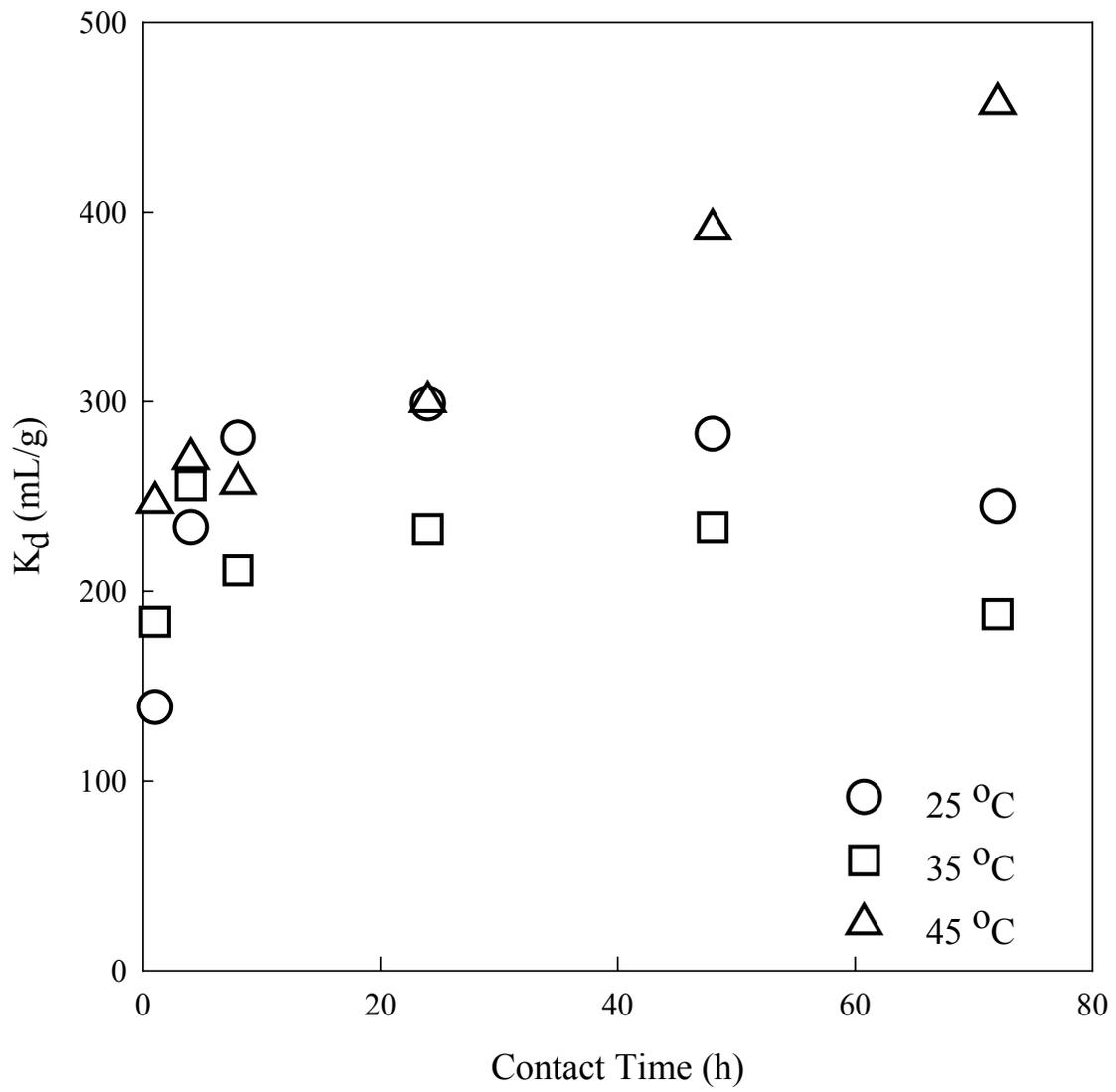


Fig. 4. Temperature effect on iron  $K_d$  as a function of time

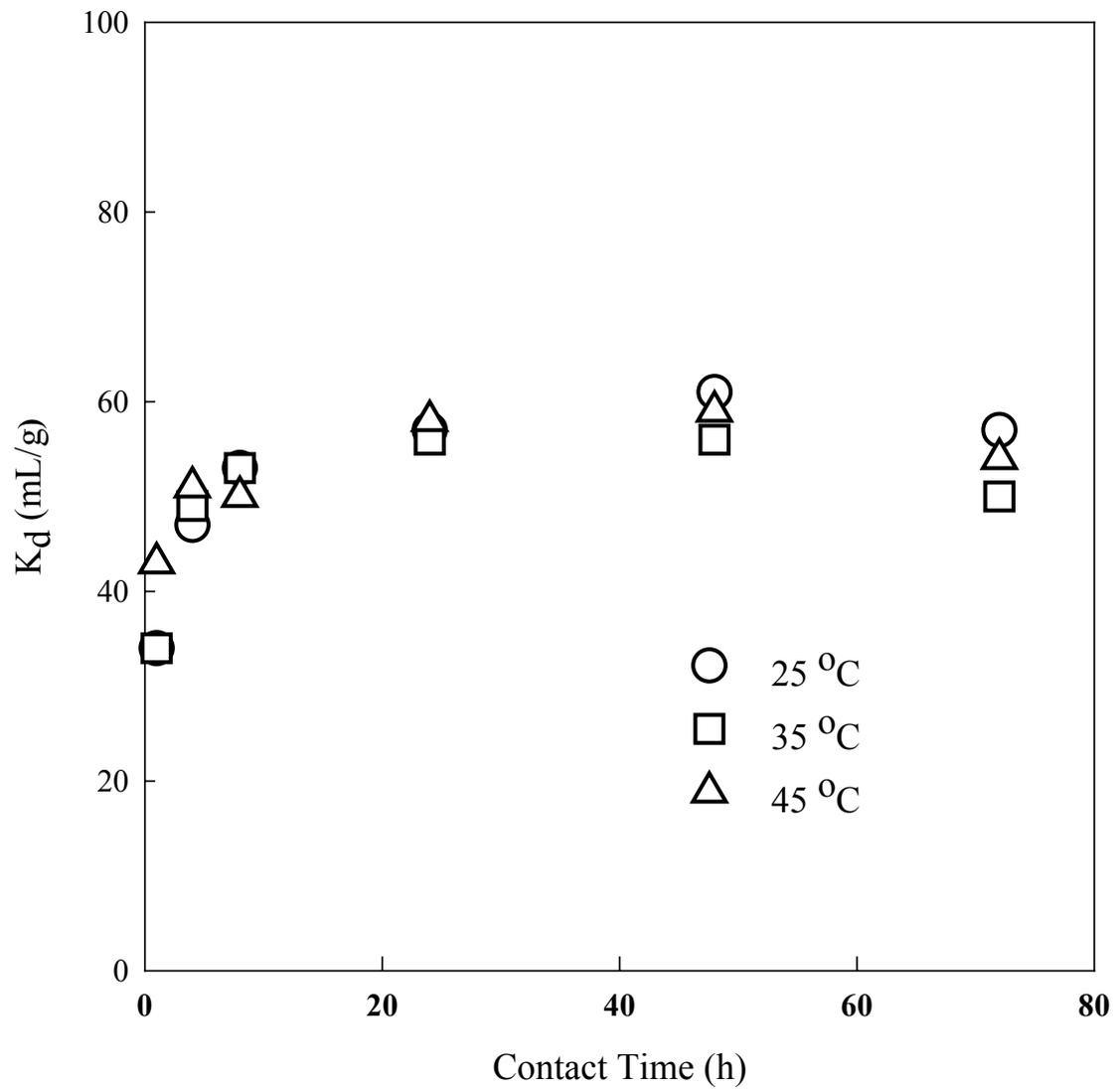


Fig. 5. Temperature effect on lead  $K_d$  as a function of time

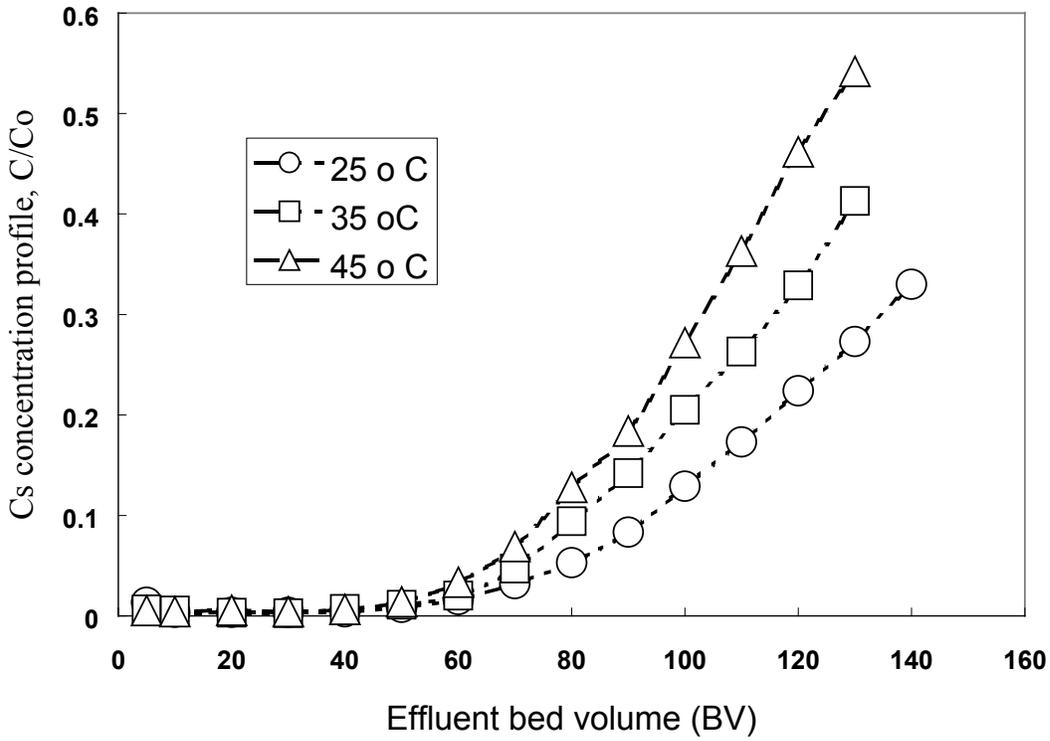


Fig. 6. Cs breakthrough curves for different temperatures

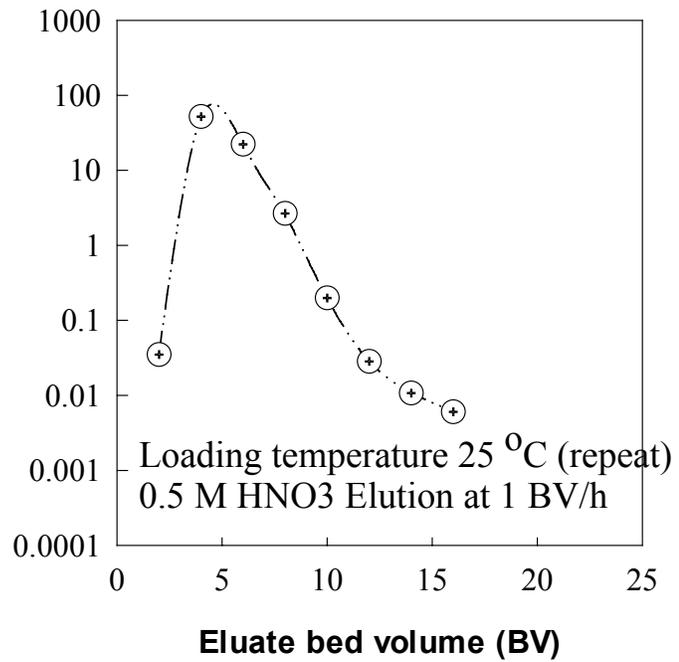
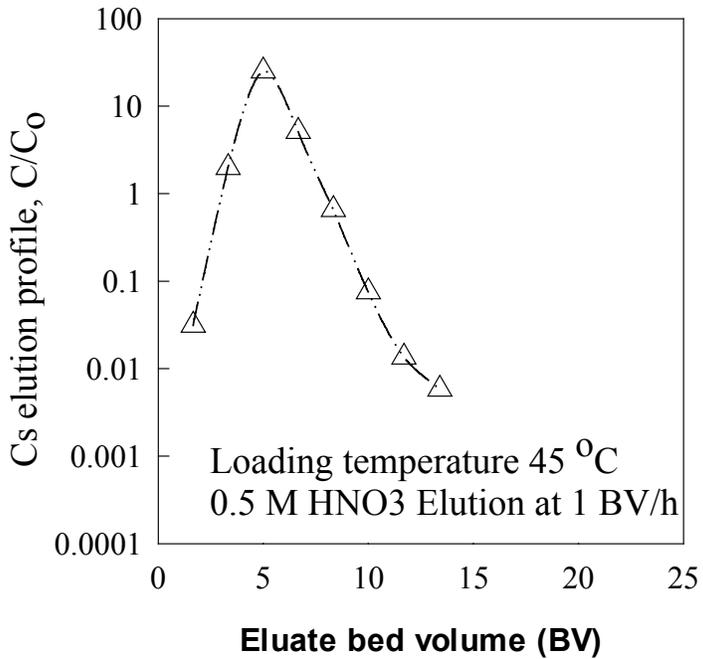
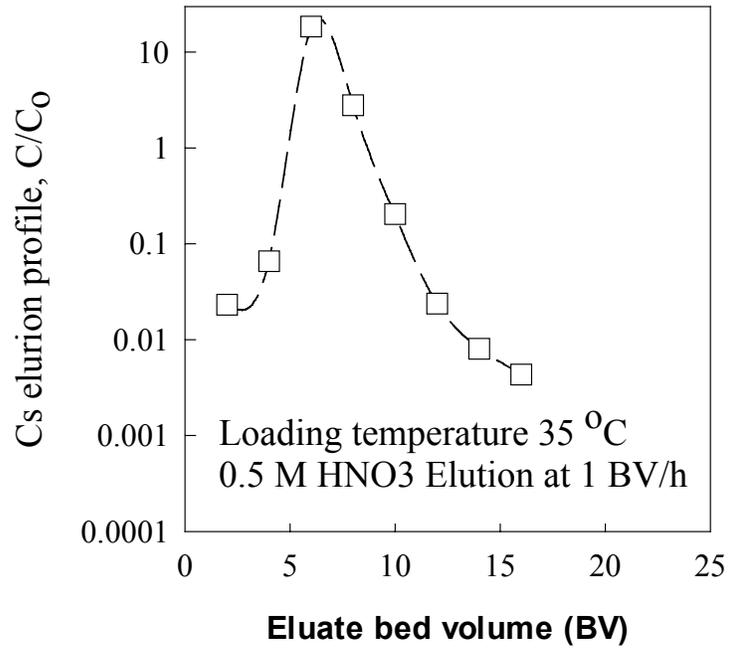
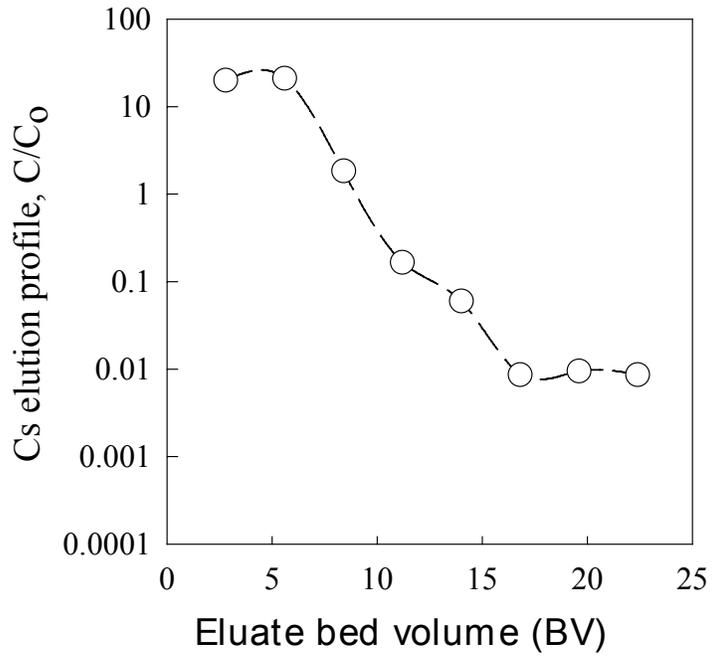


Fig. 7. Cesium Elution profiles

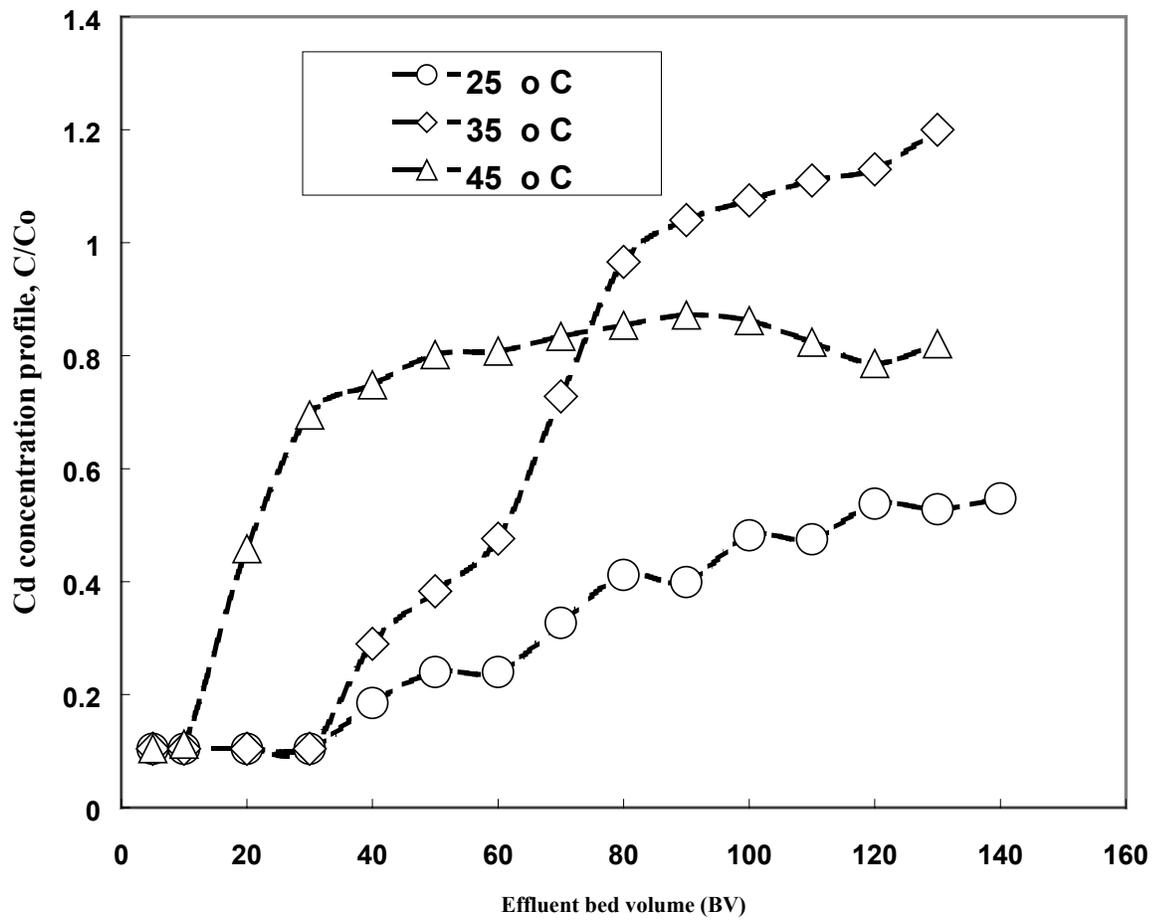


Fig. 8. Cd breakthrough curves at different temperatures

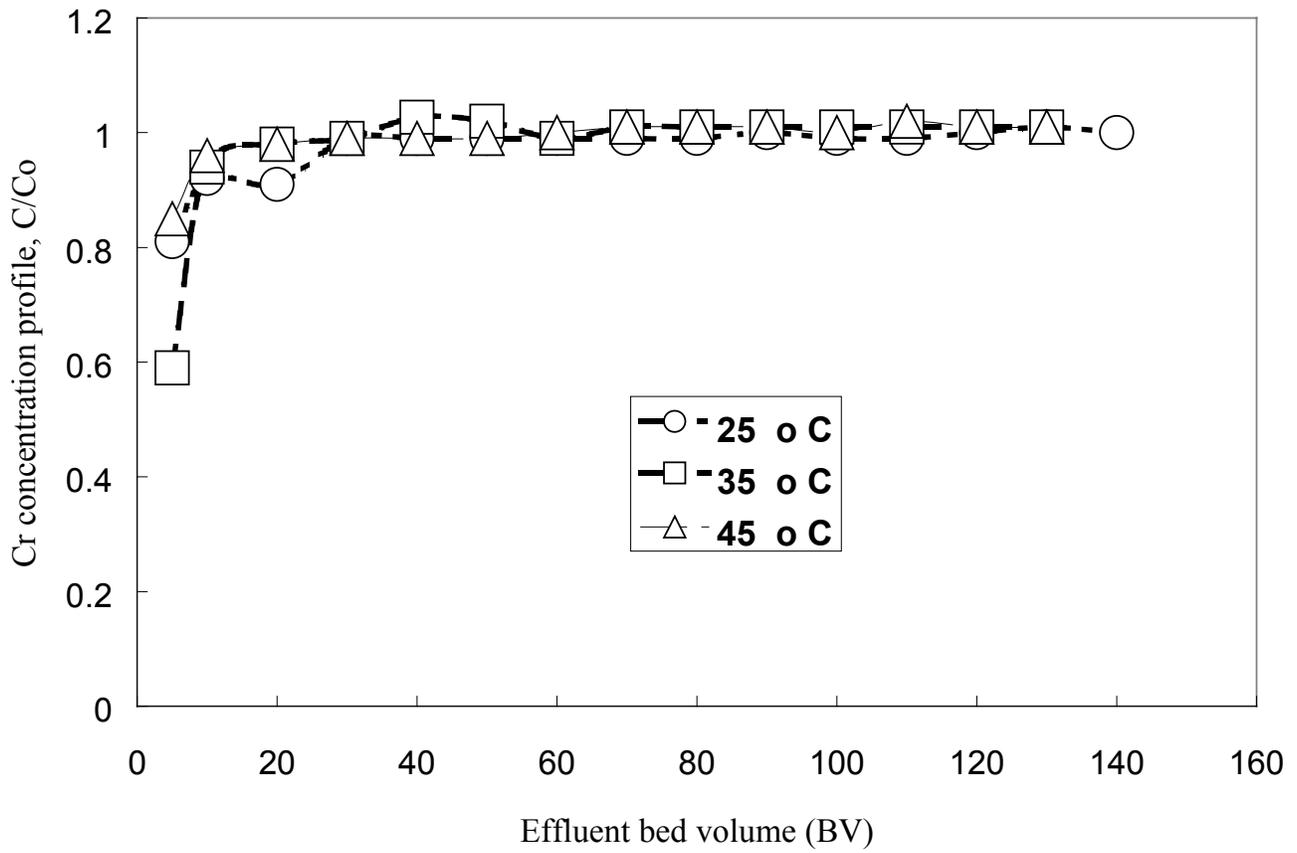


Fig. 9. Cr breakthrough curves at different temperatures

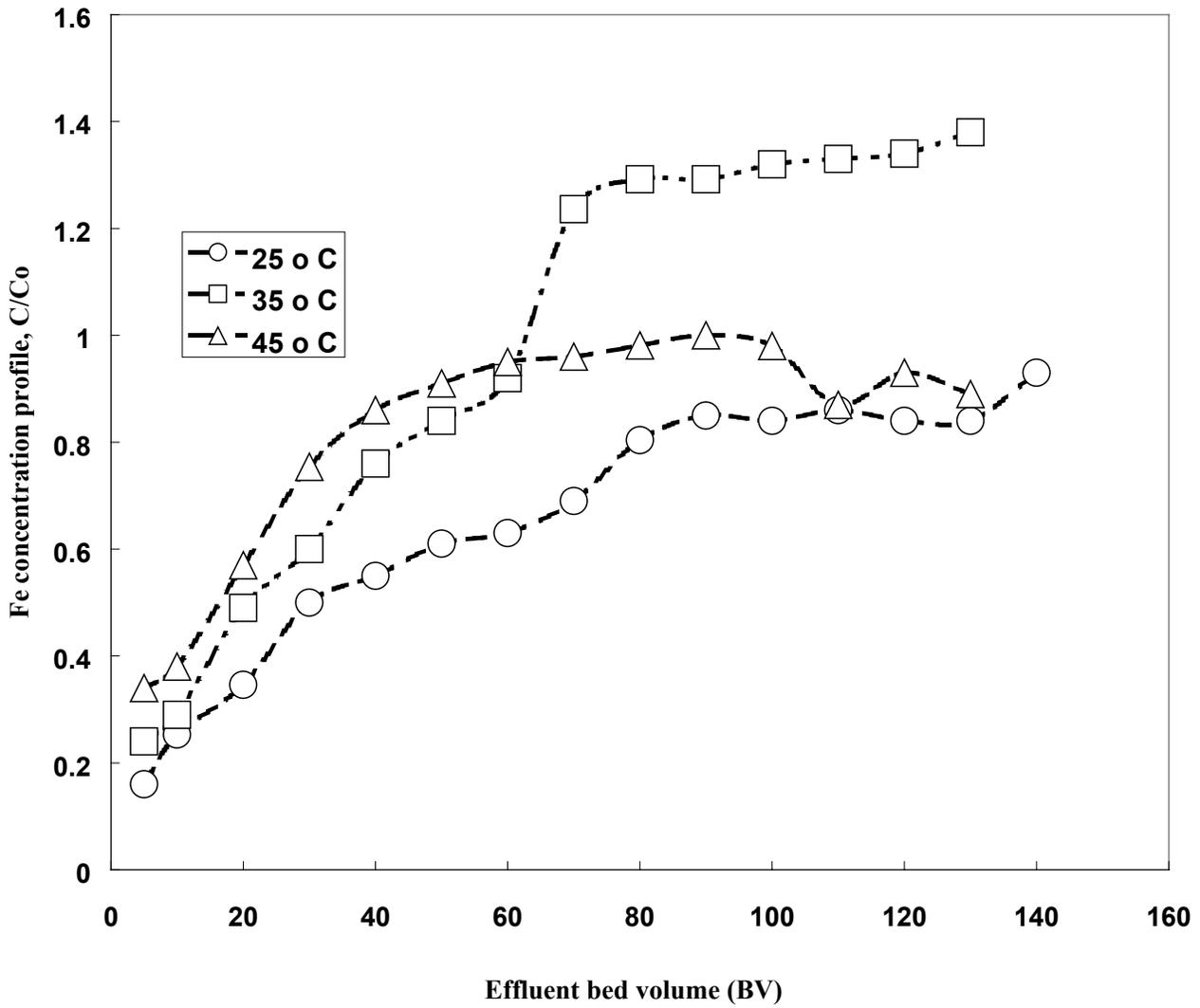


Fig. 10. Fe breakthrough curves at different temperatures

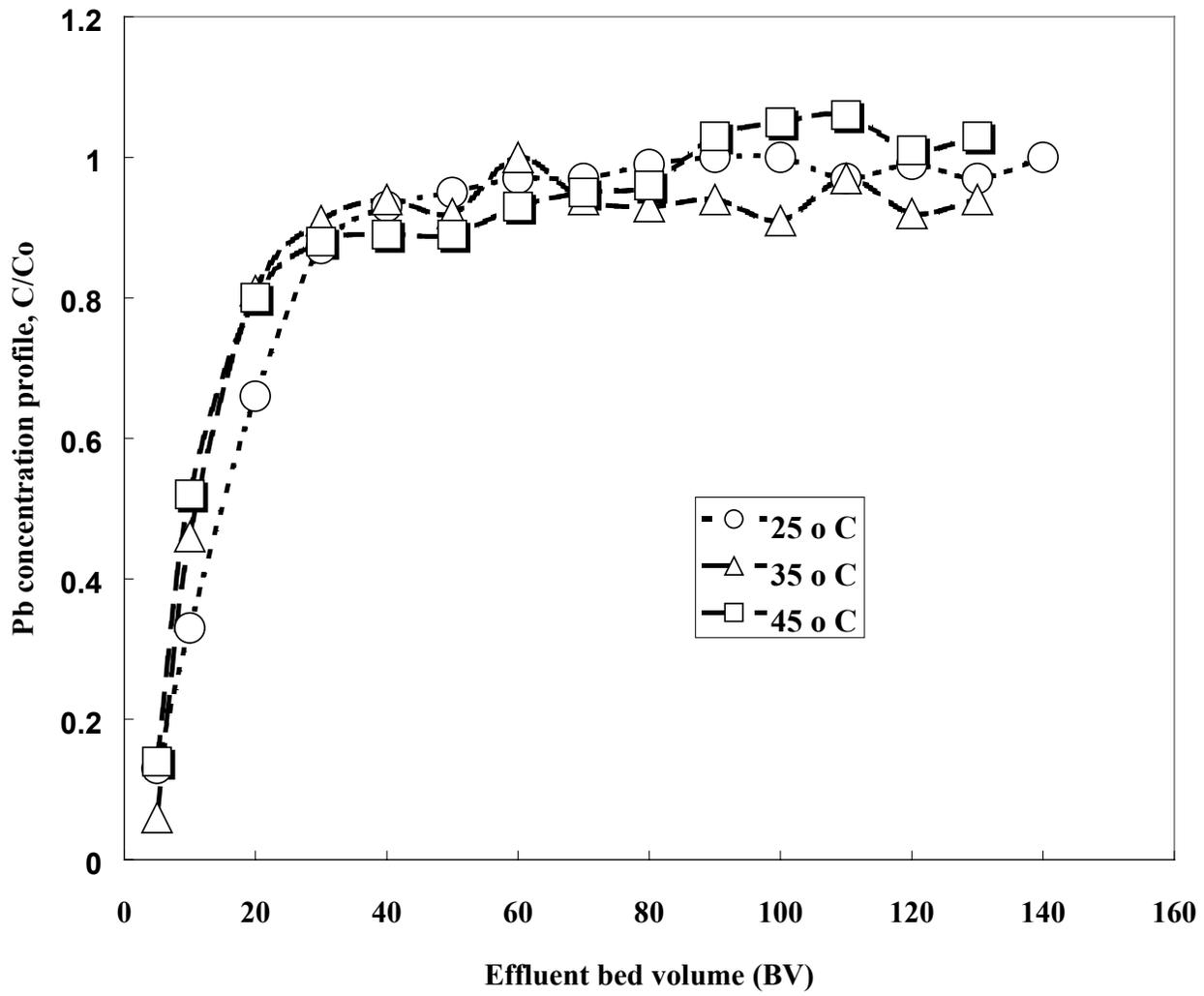


Fig. 11. Pb breakthrough curves at different temperatures

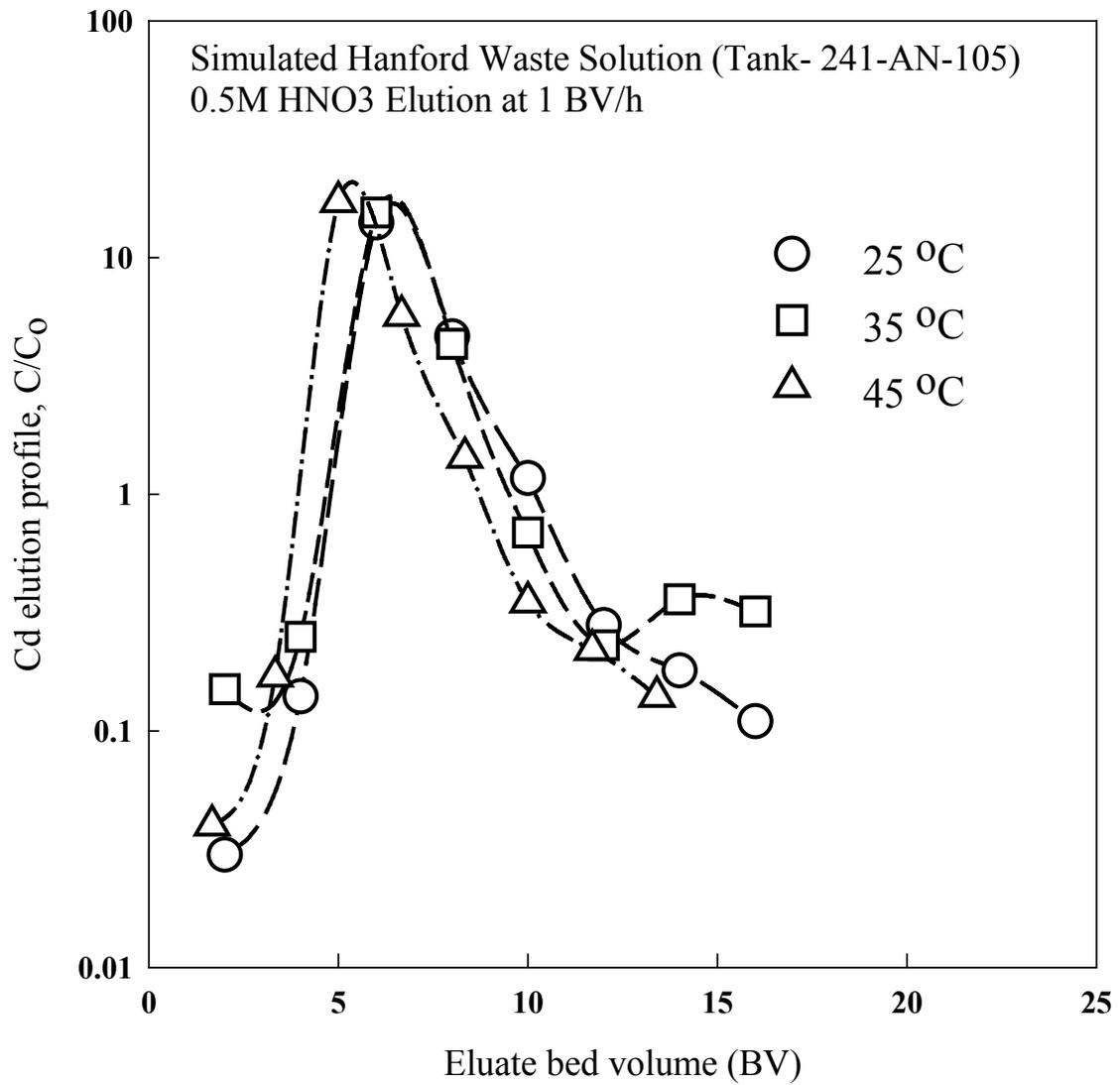


Fig. 12. Cd elution profile at different temperatures

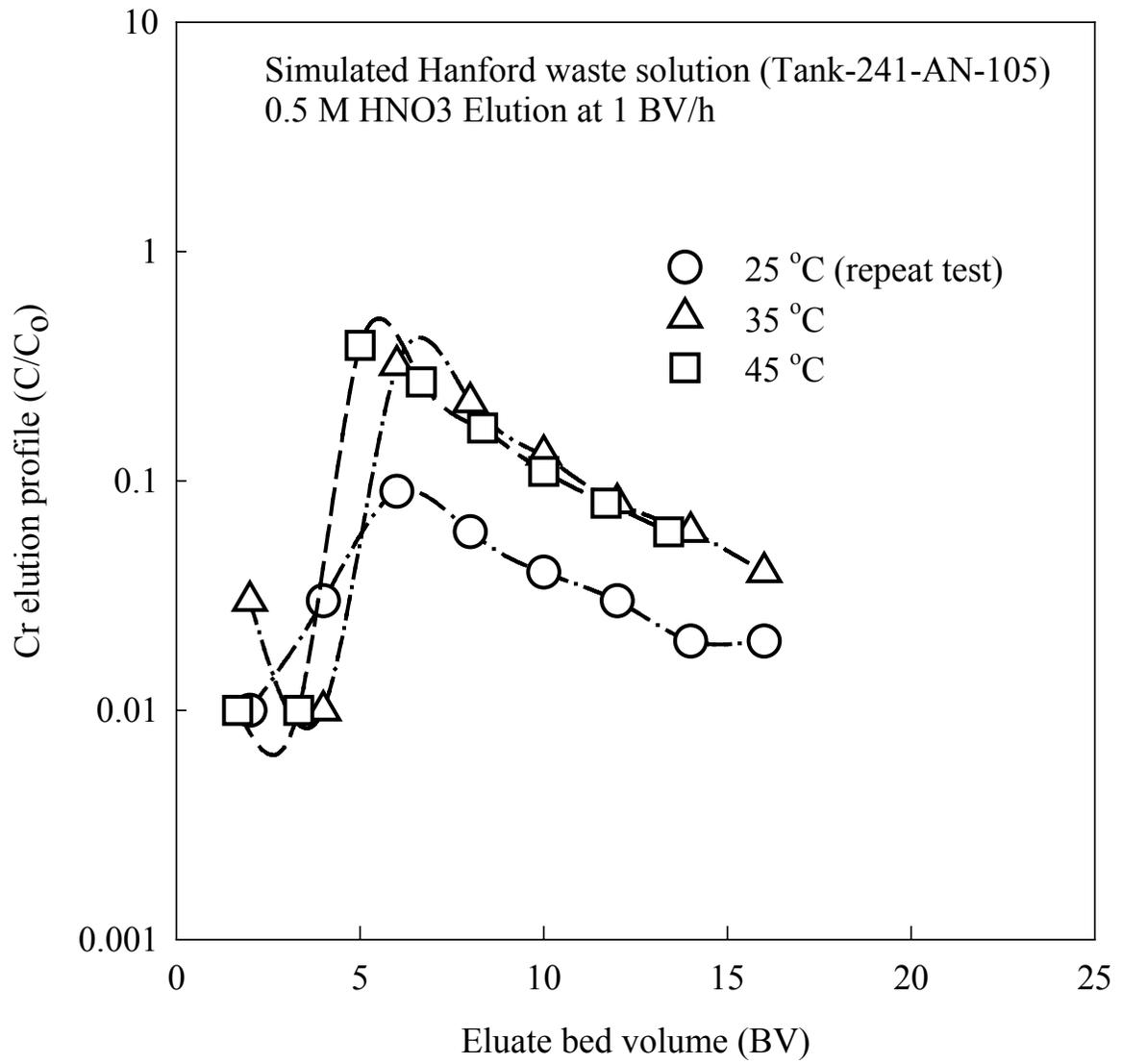


Fig. 13. Cr elution curves at different temperatures

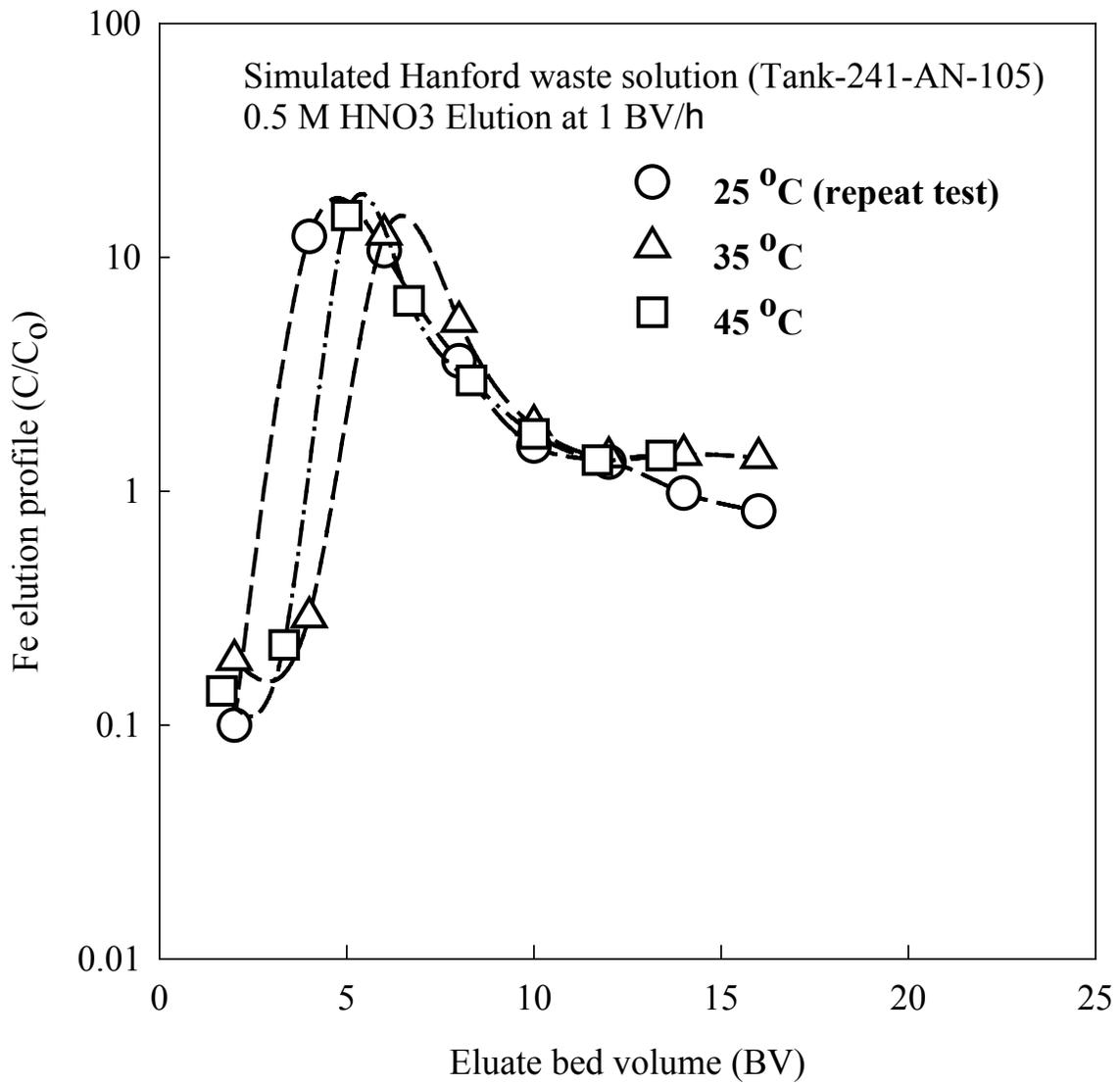


Fig. 14. Fe elution curves at different temperatures

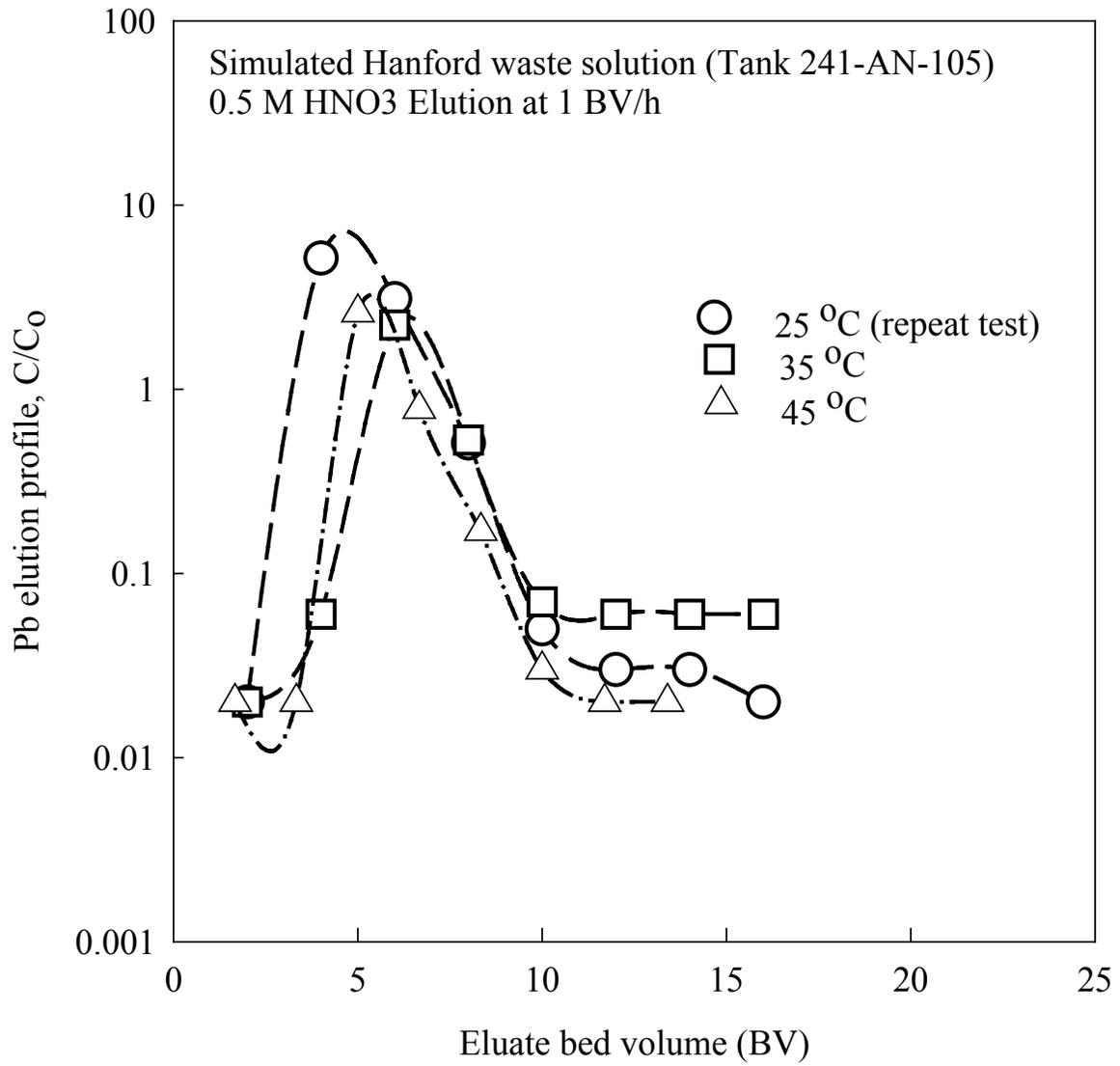


Fig. 15. Pb elution profile at different temperatures