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Recovery of radioactive cesium using nickel hexacyanoferrate as an electrically switched ion exchanger

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ABSTRACT

A combination of conventional ion exchange and electrochemical processes was conducted in production of electrically switched nickel hexacyanoferrate ion exchanger, specially used for ^{134}Cs recovery. The deposited films were physically characterized by energy dispersive X-ray spectroscopy and X-ray diffraction techniques. ^{134}Cs uptake was controlled by modulation of the ion exchanger potential in batch and flow systems. The deposited nickel hexacyanoferrate ion exchange film was found hydromechanically stable up to 130 bed volume/h. The ion uptake was about more than 90% achieved after 15 h of equilibrium. The reduced film state showed higher performance than the oxidized one in presence and absence of Na^+ ions with different concentrations. The breakthrough of the electrically switched ion exchange (ESIX) process was also conducted in different stacking of electrodes cells. Three and six stacked electrodes assemblies showed longer breakthroughs than single electrode assembly at the same operating conditions. In vertical cell, representing larger scale tests, higher concentrations (60ppm Cs^+) could be successfully treated.

KEYWORDS

Ion Exchange;
ESIX;
Electrochemical Recovery;
Ion Exchange;
Hexacyanoferrate.

INTRODUCTION

The regulations depicted in various waste management facilities include removing radioactive components, such as cesium or strontium, from fuel storage basin water or groundwater. Besides the economic importance, environmental safety emphasize on removing these radionuclides. Practically, separation and concentration of the radionuclides before vitrification would allow the bulk of the waste to be disposed as low-level waste rather than as a more costly one[1-4].

In the separation and concentration of the radionuclides before final disposal, many authors indicated that conventional inorganic and organic ion exchangers were used[5-8].

There has been considerable interest in the preparation and application of inorganic ion exchange materials in the past four decades, due to their favorable conditions in comparison with organic resins[9-12]. The advantages of these ion exchangers are their stability in acidic to moderately alkaline medium, high selectivity and resistance towards heat and ionizing radiations[12]. Besides numerous applications of ion exchange materials in radiochemical separation techniques they have also been used in the fields of industry, medicine and biology[13-16]. The main classes of materials include insoluble phosphates, arsenates, tungstates, molybdates, hexacyanoferrates (II, III) and hydrous oxides of multivalent cations[17-25].

The affinity series for monovalent ions show preferential cesium sorption for most of the cyanoferrates. Potassium hexacyanocobaltferrate which has a high selectivity for cesium is available as a cation exchanger in the form of granules[26-28]. Other ferrocyanides of copper, copper and cobalt, zinc, iron and titanium have also been found satisfactory in the isolation of cesium ions from acidic wastes, arising in nuclear fuel reprocessing[12, 14, 15, 29-31].

Although the inorganic ion exchangers are mostly resistant to gamma irradiation, they generate considerable amounts of secondary wastes from solutions used for elution, washing, and loading the exchangers. Also, the spent exchangers need to be disposed; inorganic materials typically can be used only once before disposal, and regenerable materials have short usable lifetimes[1]. In this concern, the conventional ion exchangers have to be further developed.

The electrically switched ion exchange (ESIX) technology was firstly developed at Pacific Northwest National Laboratory (PNNL). This technology provides a more economical remediation alternative[33-36]. The ESIX is mainly a combination of conventional ion exchange and electrochemistry to produce a selective, reversible procedure for ion separation, so that lower cost and secondary waste minimization is obtained. However, many drawbacks including, low exchange capacity, complex nature of the cells and electrodes, and earlier breakthroughs were noticed.

The present paper deals with both the batch and cell flow testing of ESIX systems using nickel hexacyanoferrate films deposited on high surface area electrodes. In this article, new types of electrodes rather than those used by previous authors[33-36] were selected. The electrodes are simpler so that machining of the electrodes can be carried out. Also, the deposition method of hexacyanoferrates on the electdodes was modified and compared. Batch tests were carried out to evaluate the selectivity of the nickel hexacyanoferrate material, while the flow tests were used to evaluate the feasibility of the approach as an alternative to conventional ion exchange processes. The selectivity of nickel hexacyanoferrates for cesium over sodium was examined for various sodium/cesium ratios. The effects of flow rate and initial cesium concentration on column breakthrough are reported.

EXPERIMENTAL

Materials

The electrodes used are typically platinum electrodes were supplied by The Electrosynthesis Inc, USA, having nominal surface area per volume of $40 cm^2/cm^3$ which were then coated with nickel hexacyanoferrate films. Three types with different dimensions electrodes were used. They are typically 3.0×3.0×1.0, 2.0×2.0×1.0 and 5.0×5.0× 1.0cm.

The platinum electrodes were firstly planarized with 200, 400, 600 and finally 1200 grit SiC wet/dry sandpaper. The planarized electrodes were finally polished using 1 mm Metadi diamond paste. The polished surface was allowed to contact with the specified electrolyte.

The polished surfaces were subjected to a freshly mixed solution of $2x10^{-2}M$ $NiSO_4$, $2x10^{-2}M$ $Na_3Fe(CN)_6$ and 0.25M Na_2SO_4 and application of 1.0 V potential for 300s.

Cesium nitrate and sodium nitrate were analytical grade chemicals and purchased from Sigma-Aldrich Chemical Company, USA. On the other hand, sodium ferricyanide was supplied by Fluka chemical company, Switzerland.

Radioactive cesium, namely ^{134}Cs was obtained via irradiation of 0.1g of cesium nitrate having 30 barnes cross section in the second Egyptian Research Reactor ERR-2 at Inshas site, Egypt.

Batch and flow tests

Figure (1) represents a schematic depiction of the batch and flow cell configurations used in this study; horizontal configuration (HC) and vertical configuration (VC) were used. Typically, the HC single electrode or (5 or 10 electrode assembly) was tested.

3.0×3.0×1.0cm single electrode dimensions and 2.0×2.0×1.0cm dimensions for 5 or 10 electrode assembly were applied so that the flow through the cell was bottom-up for all uptake and elution tests with solution passing through the large face of each ESIX electrode. Prior to flow testing, batch tests were conducted on each group to study their capacity and regeneration.

The other VC was a single electrode of larger dimensions. Solution flow in this cell (bottom-up) passed through the length of the 5.0×5.0× 1.0cm electrode.

A prestatic pump was used to control liquid flow through the cells at the desired rate (5–45 mL/min in HC tests; 8–24 mL/min in VC tests). Effluent samples were collected at predetermined intervals for cesium analysis.

The amounts of Na^+ released from the solid and that of Cs^+ ion sorbed by it were determined and equivalence between the two quantities was always obtained. Triplicate measurements were done and the results were found reproducible to better than ±3%. The concentration of Cs^+ ions was followed by □-activity measurements as ^{134}Cs. The scintillation assembly Nuclear Enterprises Ltd., Beenham Reading, England, with a Set of 6 scaler-timers was used for measuring □-activity, whereas Na^+ was determined using Buck Scientific Atomic Absorption, type 210 after lamp correction.

Before the onset of flow testing, batch tests were also carried out on each electrode to study film capacity and regeneration using 10^{-5}-10^{-4}M of cesium nitrate.

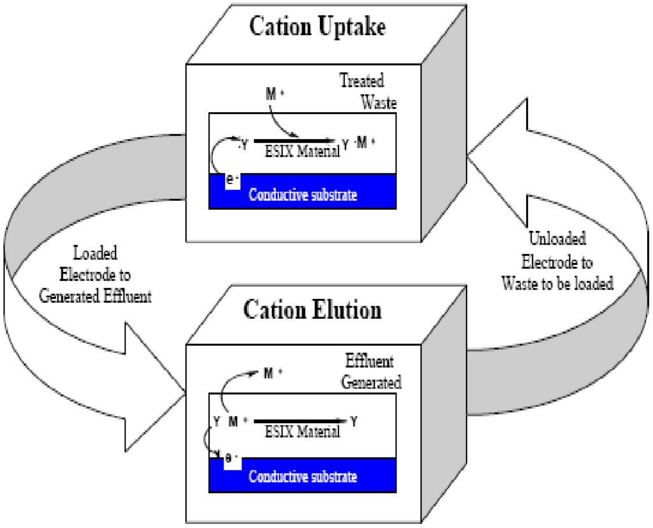

Figure 1 : Schematic depiction of the electrically switched ion exchange system used for cesium separation.

The batch testing and flow cell testing (in horizontal and vertical configurations) with a single and multiple stacked electrodes are discussed.

Characterization of the films

The different nickel hexacyanoferrate films were typically identified using energy dispersive X-ray spectroscopy and X-ray diffraction.

Energy dispersive X-ray spectroscopy (EDS)

Scanning electron microscope (JOEL JSM-5200), operated at an accelerating voltage of 15kV was used to stimulate X-ray emission. Characteristic X-ray between 0 and 10 keV were collected using Si(Li) detector with a Be window (Link systems). This permits identification of elements with Z>10. Each spectrum was acquired for 10 minutes over 1000x1000 □m region. After background subtraction via a locally weighted least-square error method, the peaks were fit to a Gaussian function using a least-square routine to calculate intensities.

X-ray diffraction (XRD)

X-ray diffraction data was acquired on all of the films cycled in mixed electrolytes and films cycled in both 1M $CsNO_3$ and 1M $NaNO_3$ in both the reduced and oxidized states. XRD glancing angle 3° 2□ experiments were performed at room temperature on spinning samples at the response. Slit widths were set so that a footprint of approximately zero point 0.15cm^2 was left on each sample. The incident excitation energy was 80000eV (□=1.55 A°). A4-circle kappa diffractometer was stepped in 0.02° increments, with an integration time of 10 seconds per point. An Oxford scintillation detector was swept from 2□ of 10° to 80°. Helium filled tubes were used along the incident beams to decrease absorption of the X-ray. The monochromator was detuned to ~75% maximum intensity to decrease harmonics.

Regeneration of the electroactive electrodes

The films can be technically regenerated by either controlled potential or controlled current methods. In this work, in situ elution of high surface area electrodes in the cell was carried out by recirculating a 1M $NaNO_3$ solution through the cell while applying a constant potential of 0.8 V. Initial testing with a single electrode was tested at a solution flow of 150 BV/h (20 mL/min), and elution lasted 5 min. A six-electrode stack was in-line eluted at a flow rate of 30 BV/h (24 mL/min) by applying 0.8 V for 20 min. When a lower concentration (0.1 M $NaNO_3$ solution) and low constant current (5mA) were used through the cell longer time is expected to elute most of the cesium exchanged on the film.

RESULTS AND DISCUSSION

Batch testing results

Cesium loading and regeneration on the electrodes was conducted in batch testing. In this concern, cesium uptake was studied with time and compared with the theoretical capacity. Figure (2) shows the results for cesium uptake by films initially in the reduced state $[Na_2NiFe^{II}(CN)_6]$ from solutions initially containing 8 ppm and 12 ppm cesium. Cesium uptake was 80–90% complete after 2h, and reached equilibrium within 15 h. Under the conditions of the experiment, cesium loading reached 24% of the theoretical ion exchange capacity. Similarly, experimental cesium capacities for nickel hexacyanoferrate powders are reported to be in the range of 23– 46% of theoretical[37].

The effect of sodium ion concentration as a competing ion on cesium ion uptake has also been investigated in batch test procedures. Figure (3) shows data for reduced films electrodes contacted with sodium-free cesium solutions and solutions containing Na/Cs molar ratios; 0.01M Na^+ and 1M Na^+ in the nitrate form were used. The kinetics of exchange was affected by the amount of sodium ion present in solution. The Sodium slowed the kinetics of cesium binding in the first two hours. However, after 24 h, nearly the same loading was observed as the case in which sodium was absent, with indication of slight loading depression in 1M Na^+ solution. Therefore it can be concluded that selectivity towards cesium ion uptake resembles that of nickel hexacyanoferrate powders[34].

According to Lilga et al., the mechanism of the ESIX could be understood in terms of current modulation through the electroactive film deposited onto a high surface area electrode[33]. Charge neutrality is the case-sensitive in forcing the ion to be adsorbed or eluted upon modulation of the potential of the film; redox reaction may occur in both cases. In case of ion loading, cathodic potential must be applied to the film which is sufficient to induce electrochemical reduction of an electroactive species, Y, and forces the ion to flow from the bulk of solution to the electrode surface as shown in Eq. (1). On the other hand, reoxidation of Y^- forces the cation to be eluted from the film to the solution as shown in Eq. (2).

$$\mathbf{e^- + \overline{Y} + M^+ \rightarrow \overline{Y^-M^+}} \qquad (1)$$

$$\mathbf{\overline{Y^-M^+} \rightarrow \overline{Y} + M^+ + e^-} \qquad (2)$$

On considering the selectivity between two different ions having the same charge, activation of the film must be taken in consideration. If the electroactive material has a greater selectivity for A^+ than B^+, the film may firstly be activated by reduction in the presence of a solution of B^+. Introducing the waste solution results in uptake of A^+ by ion exchange for B^+; B^+ is displaced into the waste solution as shown in Eq. (3).

$$\mathbf{B^+y^- + A^+ \rightleftharpoons A^+Y^- + B^+} \qquad (3)$$

In this manner, applying a cathodic potential to the nickel hexacyanoferrate film, Fe^{3+} (ferricyanide) is reduced to the Fe^{2+} state (ferrocyanide), and a cation must be intercalated into the film to maintain charge neutrality. Practically, this step must be conducted in a sodium solution as shown in equation Eq. (4). The film is then contacted with the waste solution containing cesium, which loads into the film by ion exchange for sodium, Eq. (5). Applying an anodic potential to the system, a cesium cation can be released from the film as shown in Eq. (6). This method is highly applicable, because hexacyanoferrates have very high selectivities for cesium over sodium and the electrochemistry is highly reversible in acidic and moderately basic solutions[36-39]; these films are not applicable to highly basic waste solutions because the hexacyanoferrates are highly soluble in caustics[40].

$$\mathbf{CsNiFe^{3+}(CN)_6 + Na^+\ 2e^- \rightarrow CsNaNiFe^{2+}(CN)_6} \qquad (4)$$

$$\mathbf{CsNaNiFe^{2+}(CN)_6 + Cs^+ \rightarrow}$$
$$\mathbf{Cs_2NiFe^{2+}(CN)_6 + Na^+} \qquad (5)$$

$$\mathbf{Cs_2NiFe^{2+}(CN)_6 \rightarrow CsNiFe^{3+}(CN)_6 + Cs^+ + e^-} \qquad (6)$$

Figure (3) also shows cesium loading results on an

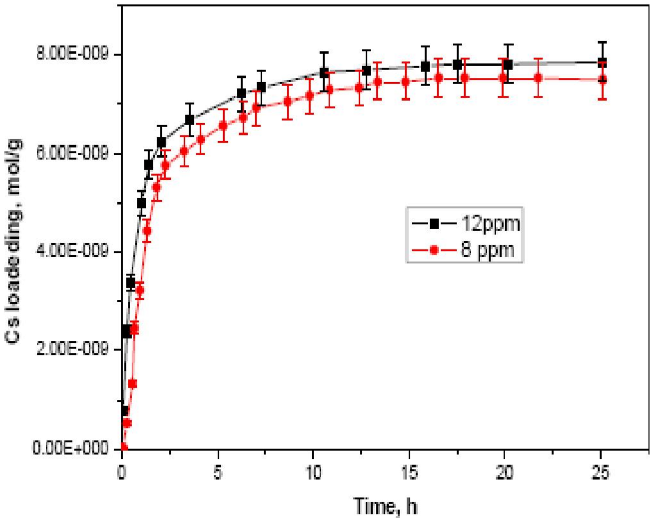

Figure 2 : Effect of contact time on cesium loading at different concentrations.

oxidized film and on an initially oxidized film with 0.1V applied cathodic potential during uptake. Without applying cathodic potential, the oxidized film, [NaNiFe^{III}(CN)$_6$], was loaded roughly with half as much cesium as in the reduced state. This variation in cesium uptake is naturally expected, as the oxidized film contains half the number of exchangeable sodium atoms as the reduced film. In that case, about 90% cesium loading was obtained compared to that of the fully reduced films in the first two hours, i.e., the applied potential accelerates cesium loading, but apparently does not affect the overall capacity of the film.

Also, in batch procedure, the unloading or elution of the exchanged cesium ion from the surface of the film was investigated. This process was found affected by both the potential applied and the conductivity of the eluting solution. In this concern, different potentials and media were tested. It was found that, conductive solutions with high ionic strength gave more efficient unloading than the less conductive media at the same potential. With +0.8V applied potential and in 1M NaNO$_3$ as an eluant, the exchanged cesium in the film was fully unloaded after 10 min. However, films were only approximately 32% unloaded in 10 ppm cesium and approximately 18% unloaded in deionized water after 15 min. After 2h in deionized water, the films were 52% unloaded. This behavior can be explained if it is considered that the more resistive solution can disperse the applied potential more than the conductive media, the driving force for metal ion unloading is reduced.

Characterization of the films

Figure (3) shows the EDS patterns for NHCF films after current modulation in different electrolytes. The film EDS analysis was used to quantify the number of moles of either sodium or cesium cations intercalated in the film. Figure (3a) represents the presence of sodium and cesium ions in the lattice of the NHCF at cathodic voltage of 0.8V. On modulation to anodic potentials of 0.20V and 0.40V as indicated in Figures (3b, c), respectively, the peaks of cesium at about 4 keV diminishes with increasing the peaks of sodium ions at about 1keV. On the other hand, peaks of iron (at ~6keV) and Nickel (at ~6-7), are still present with modulation of the voltage. Actually, cesium fully diminishes by application of 0.80V anodic potential. These results come in agreement with that observed of some hexacyanoferrates deposited by another method on nickel foam electrodes and potentially modulated from -25mV to +1125mV[41].

The X-ray diffraction spectroscopy of the same deposited films was carried out and graphically represented in Figure (4) at the same potentials. [200], [220] and [400] crystallographic diffractions were observed, which are characteristics for the NHCF structure. On the other hand, [440], [620] and [632] crystallographic diffractions were found in case of the base platinum films[41].

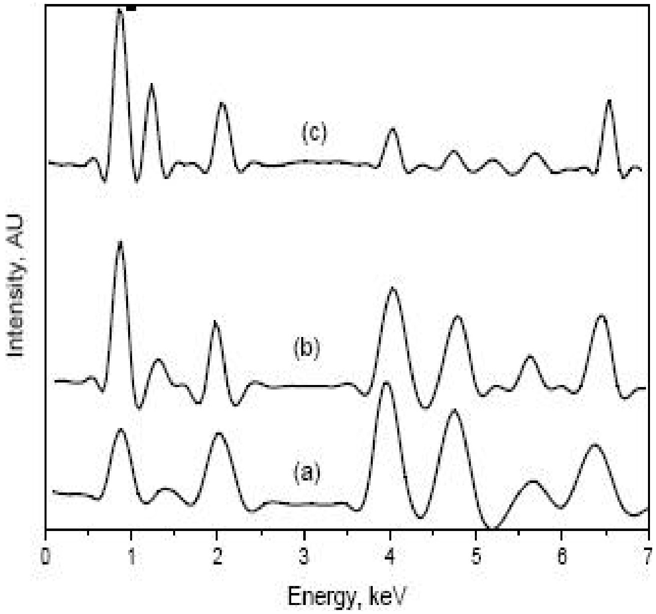

Figure 3 : Energy dispersive X-ray spectroscopic patterns of deposited NHCF films after modulation of different voltages

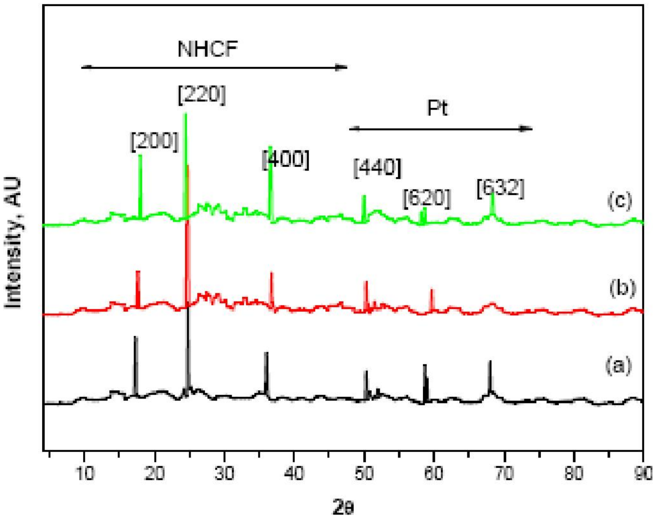

Figure 4 : X-ray diffraction patterns of deposited NHCF films after modulation of different voltages

Flow cell testing results

The flow cell investigations include the performance of hexacyanoferrate nickel electrodes for removing and eluting cesium under flow conditions. The studies were carried out in two different configurations, namely, horizontal and vertical modes using single and or stacked electrodes.

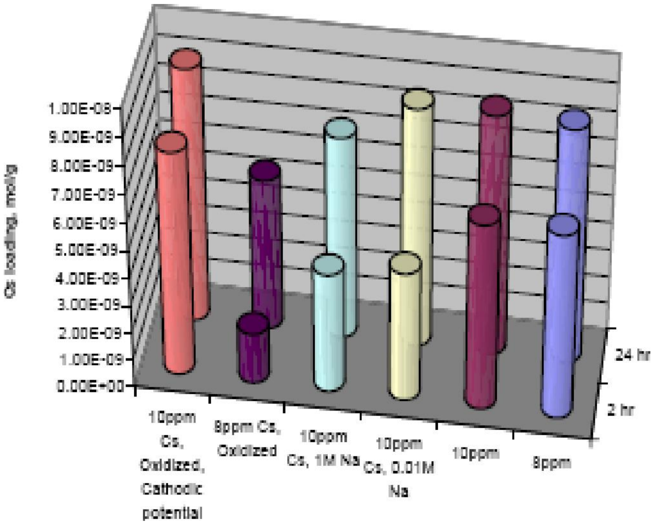

Figure 5 : Effect of added sodium and applied potential on cesium uptake in batch experiments.

Horizontal flow cell results with a single electrode

In this configuration, cesium ion uptake was identified in terms of two functions, the flow rate and initial cesium concentration, using a single electrode. The behaviors of the functions are indicated in Figures (6 and 7). Figure (6) shows breakthrough phenomenon for a feed solution containing 20 ppm cesium in different flow rates (10-130BV/h). At 10BV/h and 15BV/h, nearly similar behavior was observed till 60BV; breakthrough started at approximately 21BV and 50% breakthroughs were detected at about 50-55BV. However, faster breakthrough appeared after 60BV on using a flow rate of 15BV/h. This behavior was similarly found in the single electrode configuration when experimental slower flow rates are used. In the higher flow rates next to 15BV/h, immediate breakthrough was indicated.

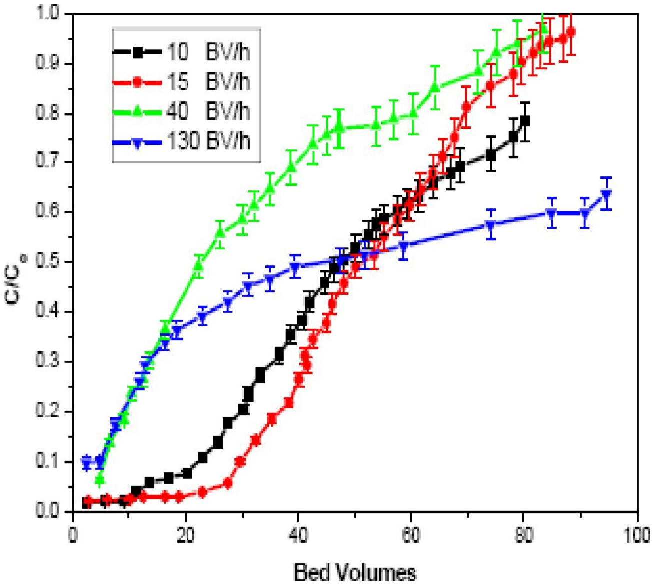

Figure 6 : Effect of flow rate on cesium breakthrough in the horizontal flow cell with a single electrode (using 20ppm Cs).

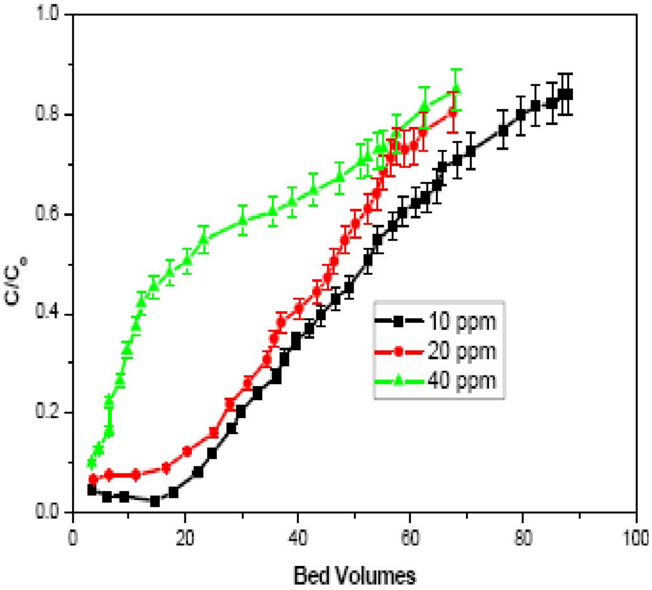

Figure 7 : Effect of concentration on cesium breakthrough in the horizontal flow cell with a single electrode (flow rate = 10BV/h).

On considering the effect of concentration on the breakthrough behavior of cesium exchange (Figure (7)), the initial cesium concentration did not greatly affect the breakthrough on using 10 and 20 ppm initial cesium concentrations at 10 BV/h (Figure 7). Breakthrough occurred rapidly at a feed concentration of 40 ppm.

The flow studies show that the films are hydrodynamically stable up to 130 BV/h, the maximum flow rate tested. No significant decline in capacity or performance was observed throughout experimentation. While a slight drop is seen in the theoretical loading in sodium solutions, where the amount of cesium loaded remains approximately constant. The drop in theoretical loading results from the normal loss in capacity after the film has been subjected to the numerous redox cycles during the course of experimentation[36]. Over the course of experimentation, the film maintained an approximately 10% efficiency in site utilization. This efficiency is approximately half that obtained in batch testing, which suggests that stacking the electrodes to give a longer bed depth may lead to improved performance and better utilization of film capacity. Films were unloaded quantitatively, as indicated both by the amount of cesium unloaded compared with the amount loaded and by the consistency of the amount of cesium loaded from one run to the next.

Horizontal flow cell results with stacked electrodes

A stacked electrode configuration was used in the horizontal flow cell to increase the effective bed depth of the cell. Stacks of three and six electrodes were tested. In three- and six-electrode stack experiments, the electrodes coated with a hexacyanoferrate film, were assembled in the cell such that solution flowed from the bottom of the cell up through the large face of each electrode in series. As a result, the bed volumes were approximately three and six times greater than that of the single-electrode experiments at the same BV/h flow rates. The concentration of cesium in the feed was 20 ppm in all tests.

Figure (8) shows the effect of the number of electrodes in the stack. The performance of the three-and six-electrode stacks was much better than that seen for a single electrode at approximately the same BV/h flow rates. For example, the best onset of breakthrough for a single electrode was 22BV obtained at a flow rate of 15BV/h; 50% breakthrough occurred at 50BV under these conditions. The three-electrode stack at a flow rate of 10BV/h operated approximately four times more efficiently than the single-electrode cell, with onset of breakthrough at 70 BV and 50% breakthrough at approximately 142BV. The breakthrough in the three-electrode stack occurs at approximately 85BV; the performance interfered with that of six stacked electrodes at about 120BV. Therefore, the performance of the three-electrode cell should be representative of performance in larger cells and used for most of the following testing and for scale-up estimates. The longer cells presumably allow for more fully developed flow, reducing channeling and dispersion.

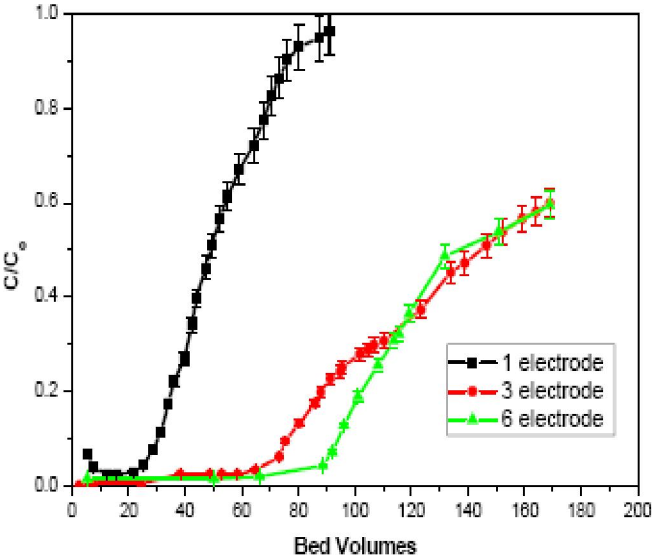

Figure 8 : Effect of number of electrodes used in horizontal flow cell testing.

The effect of flow rate on cell performance in the three-electrode stack was determined. Figure (9) shows breakthrough as a function of flow rate. The results of two initial experiments at 10 BV/h and 30BV/h are not shown because the experiments were only run for 76 BV and the collected samples contained no detectable cesium; i.e. breakthrough was not observed. In subsequent experiments conducted for approximately 150 BV, flow rate dependence was observed that was similar to that obtained in single-electrode experiments; higher flow rates gave faster breakthrough. At 90BV/h, 30BV/h, and 10BV/h, 8BV/h, 5BV/h; onset of breakthrough occurred at approximately 55BV, 73BV, 98BV, 120BV, and 133BV, respectively. Fifty percent breakthrough for 10, 30 and 90BV/h occurred at approximately 140, 120, 80BV, respectively; for 5 and 8BV/h, 50% breakthrough was not detected. At low bed volume numbers and prior to the onset of breakthrough, the column allowed approximately 1–2% of cesium to pass, i.e. C/C_o was between 0.01 and 0.02.

The continuous flow elution of a single electrode was conducted with an electrode that had previously been loaded with cesium during a breakthrough performance flow test. The process was conducted under constant potential control with 1 M $NaNO_3$ in batch recycle operation. Samples were taken from the system after different time intervals of operation at an applied anodic potential of 0.8V. The cesium elution was fast in the described method, so that it was complete within the first 5 min of operation. The amount of cesium eluted at 5, 8, 10 and 15minutes was found 32, 38 and 39 ppm, respectively. To be sure of complete elution, the electrode was taken out of the flow cell, and batch elution was conducted. It was found that no additional cesium was eluted from the electrode, indicating that all of cesium was eluted during the in-line testing. Therefore, during in-line elution, the electrode was 80% eluted after 5 min and 100% eluted after 8-9 min. Therefore, the in-line elution method was considered as effective as the batch method.

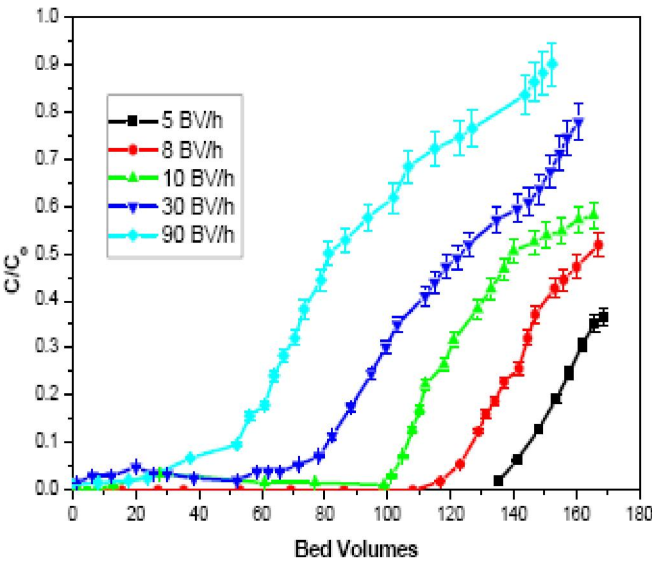

Figure 9 : Effect of flow rate on cesium breakthrough in a horizontal cell containing three stacked electrodes using 20ppm Cs).

The in-line elution was thus tested on a larger, more complex, cell. The system composed of six ESIX electrodes and six platinum electrodes, connected in parallel in the system. The flow was in the bottom-up direction through the cell previously fed with 40 ppm cesium from cesium nitrate slat solution. Generally, elution was conducted under potential control by applying a potential of 0.8 V to the entire stack for 20 min while the elution solution (1 M $NaNO_3$) was passed through the cell in batch recycle mode. It was found that, the stack can be efficiently regenerated by applying 0.1-0.8 V for 10 min while fresh 1 M $NaNO_3$ was recirculated through the cell.

To elucidate the reproducibility of the ESIX system, sequential breakthrough curves for three uptake experiments are shown in Figure (10); the first run started to breakthrough after approximately 29BV. After the first run, the entire six stack was eluted by application of 0.8 V for 20 min and regenerated in1M $NaNO_3$. Breakthrough during the second run started at approximately 8BV. After the second run, both controlled potential elution was repeated in five cycles. The performance was improved slightly in the third run, with onset of breakthrough at approximately 17BV.

As shown in Figure (10), the better performance in the first run may occur as the film on each electrode is in the fully reduced and sodium-exchanged state ($Na_2NiFe(CN)_6$). Therefore, it is possible to bind two cesium ions for each active site on the film. On the other hand, the decreased performance in the consequent runs may be explained by one of three possible scenarios. In the first, the potential distribution in the cell may be incomplete. Therefore, capacity would decrease since some of the electrodes could not participate efficiently in the ion exchange process. The second scenario proposes that, only one cesium per active site is removed. Hence, regeneration would form $NaCs\text{-}NiFe(CN)_6$, which can only remove one cesium in the subsequent uptake. The third possibility is that the eluted cesium from one electrode is absorbed by other electrodes according to the direction of flow. Therefore, in the next section, the VC was tested instead of the HC.

The determination of the exact scenario requires extended work. However, one may compare this six-stack system with the in-line elution of the single electrode, in the same configuration. The measured potential drop across the stack was only on the order of 0.002 V, suggesting that the uncompensated resistance in the cell is very small. From these, one can conclude that the second scenario is the most persuading one. The enhanced performance of the third run more than the second one can be explained by the more complete process in that case as five elution cycles were used. Also, after the first elution run, the capacity dropped to approximately half, possibly consistent with the presence of $NaCsNiFe(CN)_6$ on the film.

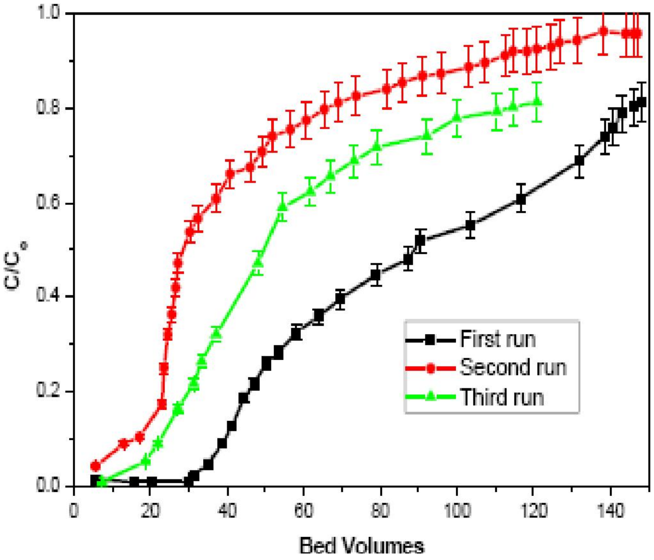

Figure 10 : Consecutive breakthrough curves for the six-electrode stack in the horizontal flow cell eluted and regenerated in-line.

Vertical cell results with a single electrode

In the vertical cell testing, the electrodes dimensions were 5.0×5.0× 1.0cm in all experiments. This configuration was used for loading-elution and regeneration of cesium in different concentrations in a larger scale procedure. The second aim of this system is to eliminate the drawbacks of the HC. A very low current (5mA) was employed to avoid possible competing electrode reactions such as oxygen evolution.

Figure (11) shows the breakthrough behavior for different cesium feed concentrations between 20 and 80ppm. Breakthrough occurred when approximately 10% of the cations in the film had been exchanged, which is similar in results of the HC. The $Na_2NiFe(CN)_6$ continued to exchange cesium after breakthrough, but the observed C/C_o increased rapidly; typically, the exchange reached 20–30% before experiments are stopped. It can be seen that, in this situation, the performance is very dependent on cesium concentration, and the electrode performance improves substantially as the concentration is decreased, which is also depends on the intercalation between the ion and the hexacyanoferrate film[41].

Eq. (6) was used to study the in situ elution of cesium from films on the nickel electrode by anodic oxidation. The initial cesium capacity was equivalent to 32 mg/g corresponding to about 40% cesium uptake, using a solution containing 80 ppm cesium. The cesium-loaded electrode was then oxidized using a constant current of 5 mA while 450mL solution of 0.1 M $NaNO_3$ was passed through the electrode at a flow rate of 2mL/s. The initial elution contained approximately 7ppm of cesium, and the total recoveries of cesium were between 80 and 85%. This may be attributed to cesium, back exchanged on the electrode. However, it would be possible to discharge most of cesium at a much higher rate, speeding regeneration, giving a higher cesium concentration in the eluant, and affording a higher concentration factor. In an advantage of this configuration, the bed performance for cesium uptake was nearly the same after each regeneration cycle, as indicated by consistent breakthrough and fractional loading in subsequent experiments.

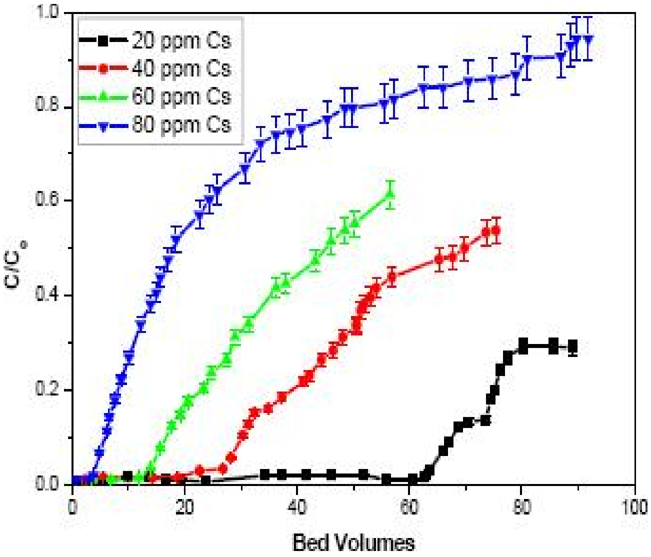

Figure 11 : Effect of feed cesium concentration on cesium breakthrough in vertical cell containing a single electrode.

CONCLUSION

The electrically switched ion exchange for cesium ion recovery was tested during this work. The possibility of cesium ion intercalation and deintercalation was emphasized by modulating the electrode potential in the positive and negative direction, respectively. This procedure can be carried out in batch and column with different assemblies. Different cycles of experiments were carried out to put the ESIX in an advantage over the conventional methods for cesium ion recovery. Also, the quantity of secondary waste was reduced in this technique, beside the regeneration of the electrodes in a simple and fast way. The new types of electrodes used as well as the preparation technique have enhanced the performance of the system so that higher hydromechanical loads can be applied. However, this work can be extended to other radionuclides, and compare the behavior of such technology with other methods for radioactive waste treatment.

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