Continuous Separation of Radionuclides from Contaminated Water by Shock Electrodialysis

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Supporting Information

ABSTRACT: The increasing popularity of nuclear energy necessitates development of new methods to treat water that becomes contaminated with radioactive substances. Because this polluted water comprises several dissolved species (not all of which are radioactive), selective accumulation of the radionuclides is desirable to minimize the volume of nuclear waste and to facilitate its containment or disposal. In this article, we use shock electrodialysis to selectively, continuously, and efficiently remove cobalt and cesium from a feed of dissolved lithium, cobalt, cesium, and boric acid. This formulation models the contaminated water commonly found in light-water reactors and in other nuclear processes. In a three-pass process, a consistent trade-off is observed between the recovery of decontaminated water and the percentage of cobalt removed, which offers flexibility in operating the system. For example, 99.5% of cobalt can be recovered with a water recovery of 43%, but up to 66% of the water can be recovered if deionization of cobalt is allowed to drop to 98.3%. In general, the energy consumed during this process (ranging between 1.76 and 4.8 kWh m⁻³) is low because only charged species are targeted and virtually no energy is expended removing boric acid, the most abundant species in solution.

1. INTRODUCTION

Nuclear waste is matter that undergoes radioactive decay, a spontaneous process by which an unstable atomic nucleus emits radiation and concomitantly transforms into smaller daughter nuclei.¹ Although radioactive decay is stochastic at the level of individual nuclei, the expected rate of decay for a collection of radionuclides can be characterized in terms of an observable decay constant such as the half life.¹ Radioactive waste is often a byproduct in the industrial generation of nuclear power and is hazardous to the environment and to nearly all forms of life. Indeed, high-energy radiation can ionize atoms or even generate free radicals (e.g., hydroxyl from radiolysis of water) that react with the cellular components of an organism, which may cause aberration of chromosomes, mutation of nucleic acids, or death of cells.²,³ Given the harmful nature of such radiation, the scientific community has sought to develop methods to isolate, manage, and dispose of nuclear waste. In this article, we adapt an emerging electrokinetic deionization method known as shock electrodialysis (SED)⁴⁻⁸ to continuously treat water contaminated with radioactive ions. This study focuses on the basic physics and design principles needed to selectively remove cobalt (⁶⁵Co) and cesium (¹³³Cs), while recovering a reasonable fraction of the water fed and minimizing the energy cost of the process. Because SED is an electrokinetic method, separation of ions is based primarily on the charge and is insensitive to mass,⁴⁻⁸ which implies that our results should also be applicable to radioactive isotopes of cobalt and cesium. The principal aim of our methodology is to concentrate nuclear waste in a contained discharge stream and, in turn, minimize the volume of waste that would need management, recycling, or disposal in subsequent processes.

Our strategy for separation is based on the phenomenon of deionization shock waves⁷ by which a sharp gradient in the concentration of salt propagates near an ion-selective surface, such as a cation exchange membrane (CEMs)⁶,⁸ or a metal electrodeposited.¹⁰,¹¹ Moreover, our system comprises a weakly charged porous medium to sustain overlimiting current—at which transport of ions is faster than by diffusion alone—as the conductivity of the solution diminishes near this surface.¹⁰,¹²,¹³ The shock wave splits the system into a region that is concentrated and another that is deionized. These regions are then continuously separated by driving flow perpendicular to the applied electric field.⁴ This system can therefore achieve electrically tunable and “membraneless”

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separation within the porous material without any physical barriers in the direction of flow. In contrast to conventional electrodialysis in which the overlimiting current is often sustained by chemical or hydrodynamic instabilities, overlimiting current in SED is sustained by electrokinetic phenomena at the scale of pores, namely surface conduction and electroosmosis. Experimentally, concentration polarization was first observed in glass microchannels emanating from nanoscopic junctions or membranes. SED, however, relies on the propagation of macroscopic shock waves across a network of charged pores, which is necessary for flow fractionation, scale-up to practical flow rates, and improvement of both desalination and water recovery by leveraging electroosmotic flow.

The first laboratory scale prototype to successfully demonstrate SED was designed, built, tested, and patented by our group. To achieve continuous operation, subsequent iterations of this system introduced a novel cross-flow architecture, in which the feed flows into a porous glass frit placed between identical CEMs, as shown in Figure 1. The frit was made of sintered borosilicate glass, a porous material with frit, the exiting NaCl, KCl, KNO3, and Na2SO4. These measurements were deionized electrolytes comprising monovalent cations, including ions based on chemical reactivity (adsorption, chelation, and precipitation), solubility and partition coefficient (solvent extraction), affinity for charged or functionalized surfaces (ion exchange, EDI), or response to electric fields in solution (EDI). Apart from SED, EDI is the only technology that involves electrochemistry, and is the only chemical method that can operate continuously without the need for additives or solvents. The remaining methods require the use of sacrificial chemicals, such as carriers or additives (adsorption, chelation, and precipitation), nonaqueous solvents (solvent extraction), or ion-exchange resins with water as multivalent ions, this result suggests that SED can be used to purify water contaminated with radioactive ions and byproducts of various nuclear processes.

2. BACKGROUND AND EXPERIMENTAL DESIGN

In treating radioactive water, the goal is often to separate the fluid into two streams. The first of these has low enough activity for safe discharge into the environment, and the second (with the smallest possible volume) is concentrated in radionuclides for further management. Existing methods for treatment can be broadly categorized into physical methods, which focus on extracting uncontaminated water, and chemical methods, which focus on extracting radionuclides. Physical methods include evaporation, reverse osmosis, nanofiltration, ultrafiltration, and microfiltration. In these methods, water is driven across an interface (either a membrane or a gas–liquid interface in the case of evaporation) that retains dissolved species in a concentrated brine. The inclusion of an excess of boric acid (commonly done in the process water of various nuclear reactors for neutron poisoning) complicates the use of several physical methods and makes them more energy intensive. This radioactively inert salt increases the osmotic pressure in membrane technologies such as reverse osmosis and is highly corrosive when concentrated. For these reasons, selective removal is preferable to indiscriminately concentrating all dissolved species.

Chemical methods, which are typically (but not always) selective in molecular separations, include solvent extraction (using liquid phase compounds), precipitation, chelation, ion exchange, and electrodeionization (EDI, sometimes called hybrid ion-exchange electrodialysis). These methods target ions based on chemical reactivity (adsorption, chelation, and precipitation), solubility and partition coefficient (solvent extraction), affinity for charged or functionalized surfaces (ion exchange, EDI), or response to electric fields in solution (EDI). Apart from SED, EDI is the only technology that involves electrochemistry, and is the only chemical method that can operate continuously without the need for additives or solvents. The remaining methods require the use of sacrificial chemicals, such as carriers or additives (adsorption, chelation, and precipitation), nonaqueous solvents (solvent extraction), or ion-exchange resins with water.
regarding acids and salts (ion exchange), the disposal of which has been deemed challenging.31,34

In LWRs (see Figure 1 for a simplified schematic), the most common and active byproducts include cobalt-60 and cesium-137.35,36 Cobalt-60 is the main contributor to high levels of radiation because it has a short half life (5.3 years) and emits high-energy gamma rays (1.17 and 1.33 MeV).35 Cesium-137, on the other hand, has a longer half life (30 years) and is not as active as cobalt-60 but it is one of most abundant radionuclides produced from fission of uranium-235.36,37 Moreover, this species poses long-term risks because, like cobalt-60, it produces high-energy beta particles and gamma rays.38 Cesium in general is an alkaline metal that becomes a monovalent ion in solution and is chemically similar to sodium and potassium. Radioactive cesium is therefore readily taken up by biological organisms, in which it can deposit on soft tissue and, over time, induce thyroid cancer.39,40 Cesium-137 has been deemed difficult to remove because of its small radius of hydration and high (mass) diffusivity.36

In this study, we prepared model radioactive water (referred to hereafter as "practical water") with the composition outlined in Table 1, as proposed by our sponsor, Mitsubishi Heavy Industries. This solution includes nonradioactive isotopes of the ions most abundant and active in the process water of LWRs, namely cobalt and cesium.35,36 Boric acid is included abundantly as it is often used as neutron poison in these reactors because boron-10 can reduce the likelihood of thermal fission by absorbing neutrons.24 Last, lithium-7 is used (in the form of LiOH) as an additive to control water chemistry and minimize the corrosive effects of boric acid.39,40 During operation, small amounts of hazardous corrosion and fission byproducts (e.g., cobalt and cesium) are released into the process water, such that nonradioactive species may undergo radioactivation near the hot reactor core.56,41-43 (e.g., cobalt-60 is produced when its precursor, cobalt-59, is bombarded with thermal neutrons; cobalt-59 is the naturally occurring isotope of cobalt with 100% abundance, and it is used in alloys that are required to possess thermal and mechanical resilience44). These species are then able to settle onto surfaces of the cooling system and recirculation pipes, and the quantity of undesired deposits of radionuclides increases with time.31,45 Accumulation of radioactive matter in the structural portions of nuclear reactors is thus an occupational hazard to those who work in the vicinity of these systems and are exposed to such radiation. We note, however, that demineralization of process water in LWRs is only one possible application of SED, and the study of selective removal of cobalt and cesium is generally relevant to treatment of nuclear (waste)water.20,21,46,47

### Table 1. Concentrations of Prevalent Species in Practical Water, the Nonradioactive Analog of Contaminated Process Water in Nuclear Reactors

<table>
<thead>
<tr>
<th>species</th>
<th>concentration (ppm [mM])</th>
<th>role</th>
</tr>
</thead>
<tbody>
<tr>
<td>boron</td>
<td>4000 [370]</td>
<td>present in boric acid; boron-10 serves as neutron poison44</td>
</tr>
<tr>
<td>lithium-7</td>
<td>2.2 [0.32]</td>
<td>used (as LiOH) to stabilize pH and control corrosion49</td>
</tr>
<tr>
<td>cobalt-59</td>
<td>20 [0.34]</td>
<td>cobalt-60 is the main contributor to high levels of radiation55</td>
</tr>
<tr>
<td>cesium-133</td>
<td>100 [0.75]</td>
<td>cesium-137 is one of the most abundant fission byproducts56</td>
</tr>
</tbody>
</table>

3. MATERIALS AND EXPERIMENTAL METHODS

The device used here was based on a design recently published by our group.39 This continuous, laboratory scale architecture is illustrated in Figure 2. Our device included three inlets, two to transport fluid to the electrodes and a third to deliver contaminated feed, and four outlets, two to transport fluid from the electrodes and the other two to generate fresh and brine streams at the splitter. All fluids were transported through 1/8th in. Tygon tubing (Saint-Gobain) glued onto portplates made of cast acrylic. These portplates were used to seal liquids inside the device and to support the rubber tubing in which fluid flows. Moreover, four 1/16th in. Viton rubber gaskets (DuPont) were used to conformally seal the device and simultaneously provide channels for the electrode solutions.
(catholyte and anolyte). The electrodes in this device were platinum meshes (Sigma-Aldrich) that were connected to a Gamry Reference 3000 potentiostat/galvanostat using titanium wires (Alfa Aesar). The electrodes and wires were secured in place by compressible Viton gaskets. CEMs (Naflon N115, Ion Power) with a thickness of approximately 130 μm served as fluidic barriers between the electrode channels and the porous medium, which in this study was a borosilicate frit (Adams & Chittenden Scientific Glass) with ultrafine pores (nominally ranging from 0.9 to 1.4 μm in size), an internal surface area of 1.75 m² g⁻¹ based on Brunauer–Emmett–Teller theory, a mass density of 1.02 g m⁻³, a porosity of 0.31, and dimensions of 0.9 cm × 2 cm × 1 cm. Prior to assembly, the frit was glued onto an acrylic frame using Devcon 2 Ton Epoxy (McMaster-Carr). The splitter (placed midway down the frit for ease of assembly) was made of cast acrylic and was sealed against the top face of the frit using the 0.04 in. GORE expanded polytetrafluoroethylene gasket tape. Holes in all of the acrylic slabs and rubber gaskets were formed using a laser cutter (Universal Laser Systems) and refined with a drill press (Palmgren 10 in., 5-speed bench model). These layers were then stacked and held together with nuts, bolts, and washers made of 316 stainless steel.

To prepare practical water with the composition shown in Table 1, we formulated stock solutions with 1000 times the target concentrations made from lithium hydroxide monohydrate (LiOH·H₂O), cobalt(II) chloride hexahydrate (CoCl₂·6H₂O), and cesium chloride (CsCl). Appropriate volumes of these solutions were then diluted in deionized water, followed by the addition of solid boric acid (H₃BO₃) to achieve a concentration of 370 mM. (All reagents were purchased from Sigma-Aldrich and used as received). We note that H₃BO₃ is a weak acid with a pH of practical water, the dynamics of proton transport, and composition of cations. Conductivity and pH were measured using Mettler Toledo analytical instruments (SevenCompact pH/Cond S213), and composition was determined using inductively coupled plasma mass spectrometry (Agilent 7900 ICP–MS). The plasma in ICP–MS was made from argon gas and was supplemented by helium, which is normally needed to analyze elements with high ionization energies (e.g., Co) for which argon plasma alone is not a sufficient source of ionization. To improve the accuracy of our data and subsequent analysis, we incorporated an internal standard that introduced 100 ppb of indium to all of our samples. Because the output of ICP–MS was numerical (in counts per second), quantitative analysis required calibration of the measurements, which was achieved by processing a set of reference standards and producing a calibration curve, an example of which is shown in Figure S1 (Supporting Information). These standards (Li, Co, Cs, and In) were purchased from Sigma-Aldrich and serially diluted to prepare a set of samples encompassing the concentrations relevant to this study. All samples and standard solutions were diluted in 2 vol % nitric acid prior to analysis by ICP–MS.

4. RESULTS AND DISCUSSION

4.1. Principles and Performance of SED. The key phenomenon that governs deionization in SED is propagation of a shock wave across which concentration varies drastically and a depletion zone is formed. This shock is generated by providing the system with an overlimiting current, which is current in excess of the flow-limited current (Iₐₘᵢₙ) defined as

\[ I_{\text{lim}} = \sum_i n_i C_i F' Q' \]

where \( n \) is valence (charge), \( C \) is molar concentration, \( F \) is Faraday’s constant, \( Q' \) is the volumetric flow rate of the feed,
and the sum is taken over all cations \( k \). This definition of \( I_{\text{lim}} \) can be interpreted as the rate of forced convection of positive charge carriers into the device, and it was assumed that the flux of anions is 0 at steady state in the presence of ideal CEMs. Using the composition of practical water in Table 1 and with \( Q' = 0.065 \, \text{mL min}^{-1} \), we found that \( I_{\text{lim}} = 180 \, \mu\text{A} \). We verified this value experimentally by performing a conventional voltage sweep from 0 to 10 V and measuring the current, as shown by the \( I-V \) curve in Figure S2 (Supporting Information). After exceeding \( I_{\text{lim}} \), the (overlimiting) current increased linearly with voltage and effected constant conductance, which was consistent with the governing theory and previous experimental observations in negatively charged porous media.4,12

Based on a previous study by our group, we operated our SED system in galvanostatic mode (see Figure S3 in the Supporting Information) because it facilitates the formation of

Figure 3. Quantitative analysis of the deionization of (a) lithium, (b) cobalt, and (c) cesium in practical water. Upper (lower) half of each panel shows the measured concentration and calculated deionization (enrichment) in the fresh (brine) stream as functions of dimensionless current. Concentration of ions in the feed was 1.41 mM, with compositions outlined in Table 1. Each data point represents the arithmetic mean of four samples, and the shaded areas correspond to the range of those samples.

Figure 4. Quantitative analysis of the WR and energy demand/cost corresponding to the results shown in Figure 3. (a) WR as a function of dimensionless current; graduated cylinders portray relative proportions of the fresh and brine products, and each data point represents the arithmetic mean of four samples with the shaded area corresponding to the range of those samples. (b) Power and cost rate as well as (c) energy density and cost density as functions of dimensionless current; cost rate (cost density) is equal to power (energy density) multiplied by the residential cost of electricity, which varies between states in the US. (d) Cartoon schematic to aid with visualization of the cost needed to apply three times the dimensionless current to a body of water with volume equal to that of the Prudential Tower in Boston, MA; CD is cost density from (c).
a stable deionization shock wave when supplying overlimiting current. (Potentiostatic operation, on the other hand, tends to result in overshoot and oscillation about a desired overlimiting current and is associated with variability in the shock wave). Our results for treatment of practical water are presented in Figure 3, where deionization (the percentage removed of a given species, DI) is defined as

\[ DI = 100% \times \left(1 - \frac{C_{\text{fresh}}}{C_{\text{feed}}}\right) \]  

(5)

enrichment factor (EF) as

\[ EF = \frac{C_{\text{brine}}}{C_{\text{feed}}} \]  

(6)

and dimensionless current (\(\bar{I}\)) as \(\bar{I} = I/I_{\text{lim}}\). The upper half of this figure illustrates that the concentration of cations (Li\(^+\), Co\(^{2+}\), and Cs\(^+\)) in the fresh stream decreased—by up to 92% for both Co\(^{2+}\) and Cs\(^+\)—with current. Moreover, the lower half shows that the concentration of cations in the brine stream increased with current. Deionization that occurred with no applied current was most likely due to exchange of H\(^+\) (abundant in the cathode) with cations in practical water across the lower membrane.

4.2. WR and Energy Cost. Given the importance of WR and energy efficiency in desalination systems, we analyzed the recovery ability and energy demand of SED when used to treat practical water. WR, sometimes referred to the recovery ratio, is defined as

\[ WR = \frac{Q_F}{Q_W} \]  

(7)

where \(Q_F\) is the volumetric flow rate of the fresh stream, and it is shown in Figure 4a to increase (up to 80%) with current. This increase in WR is predominantly due to electroosmotic flow (see Figure 3d and the Supporting Information in ref 4); the position of the splitter was not changed in this study, although it could be adjusted in future designs for improved WR. Analysis of the electrical energy needed for deionization is shown in Figure 4b,c, where power \(P = \text{product of applied current and (steady) voltage}\), and energy density \(E\) is power divided by the volumetric flow rate of the feed. Although electrical power is the more natural measure of energy transport, it is extensive and does not scale with the size of a system (particularly with flow rate). Energy density is therefore of greater value in quantifying the energy efficiency of SED. In treating practical water, the energy density increases quadratically with current, though it was on the order of 1 kW h m\(^{-3}\) for dimensionless currents between 3 and 5. Moreover, the cost of fluidic pumping in our laboratory scale system was negligible compared to the cost of electrical energy.
which electricity is expensive (MA, $0.21 \text{ kW h}^{-1}$ respectively, multiplied by the cost of residential electricity per Figure 4c), which are equal to power or energy density, of SED is to consider the cost rate (Figure 4b) or cost density electrodes), and Li+, 91% of Co2+, and 85% of Cs+) to a body of water with a times the dimensionless current (enough to remove 82% of Water Reactor, requires coolant at a volume equal to that of the Prudential Tower in Boston, MA. For comparison, a nuclear reactor with an electrical power output of 1.7 GWe, such as the US Advanced Pressurized Water Reactor, requires coolant at a flow rate of approximately 28 m$^3$ s$^{-1}$. This flow rate corresponds to 8.8 $\times$ 10$^8$ m$^3$ (>1500 times the volume of the Prudential Tower) of water that passes through the reactor core annually. The simple economic analysis introduced here will be useful when SED is being scaled up for use at commercial scale.

4.3. Implementation of a Multistep Process. For common desalination technologies, performance is improved and energy consumption is reduced by using multiple units or stages of the technology in series and by operating each stage at lower power. Such an approach is especially suitable for SED because power increases quadratically with current (Figure 4), even though deionization eventually plateaus (Figure 3). To demonstrate this claim, we developed a new configuration for our system that involved a 3-step process for deionization of practical water. Because the throughput of our laboratory scale device was low, we accelerated experimentation with this process by feeding serially diluted solutions in turn to the same device. A dilution factor of 5 was chosen for the second step and 25 for the third based on deionization of the target species in the first two steps at a dimensionless current of 5. In other words, concentrations of the feed to each pass were 1.41, 0.282, and 0.0564 mM, neglecting boric acid. In Figure 5a, we present two-dimensional arrays of deionization for each species as a function of dimensionless current in each pass. In these experiments, dimensionless current ranged from 1 to 20, though deionization typically plateaued at some intermediate value. To examine the performance of our system at one such value, we report deionization per pass and cumulative deionization for each species at a dimensionless current of 5, as shown in Figure 5b. In the first and second passes, all three species were removed in nearly equal proportions, whereas in the third pass, Co2+ was preferentially removed (see Figure S4 in the Supporting Information for discussion of this observation). This selective separation of the divergent ion agrees with a previous experimental study by our group, in which magnesium was selectively removed from an aqueous mixture of NaCl and MgCl$_2$. Figure 5b also shows that our 3-step process led to a high cumulative deionization for each species, ranging from 96.3% for Cs$^+$ to 99.6% for Co$^{2+}$. Based on its ability to remove target ions from practical water, SED could function as a novel method for treatment of radioactive waste.

In addition to removal of target ions, effective methods for decontamination of water must also be optimized for total deionization, WR, and energy density. These quantities are shown for our 3-step process in Figure 5c and are consistent with the previously observed trends: total deionization often plateaus at some moderate value of dimensionless current, whereas WR and energy density increase monotonically with current. It is striking to learn that our device can sustain WR at over 92% ($I = 20$) primarily by electroosmotic flow and even though the splitter is positioned midway along the width of the filter. Moreover, successive steps in this process contribute little energy in addition to that consumed in the first step (see Figure S3 in the Supporting Information), which implies that a contaminated feed can be repeatedly passed through the device for greater deionization at a reduced cost. This proportionality between energy demand and concentration of the feed—even in the dilute limit—gives SED an advantage over conventional purification techniques, which typically require an input of energy that is bounded from below as the feed becomes more dilute. As with other desalination methods, removal of more ions by multistep SED comes at the expense of water recovery, which diminishes in every pass. We will address this challenge in future generations of our device by introducing a recycle scheme that feeds the brine stream from a later pass back to an earlier pass the feed to which is of comparable concentration.

So far, we quantified the ability of SED to remove target species from practical water and identified general rules to optimize the design of a real system that can treat nuclear waste. In particular, we inferred a complex coupling between the extent of deionization—convoluted by the selective nature of separation by SED (Figure S4 in the Supporting Information)—WR, and energy demand. The relationship between these parameters is nonlinear, and indeed, we observe quadratic growth in energy density with applied current (Figures 4b,c and 5c). Moreover, deionization varies between species and is not monotonic, and WR appears to increase sublinearly with applied current (Figures 4a and 5c). These results suggest that there is an inherent trade-off between deionization, WR, and energy efficiency, which poses a significant challenge in satisfactorily treating nuclear waste while minimizing the demand for power. We addressed this challenge from the perspective of systems engineering by introducing a new figure of merit ($\Psi$) defined as

$$\Psi = D I^2 \times \text{WR}^n \times f(\hat{E})$$

where DI is deionization (squared to emphasize this metric), WR is water recovery, $n$ is a positive integer (either 1 or 2 here), and $f(\hat{E})$ is a dimensionless function of energy density that ranges from 0 to 1. This function may be constant

$$f(\hat{E}) = 1 \text{ (no penalty on energy demand)}$$

linear
Introducing a figure of merit allows us to quantitatively decide which operating conditions in each pass maximize deionization in our system. Characterization of the performance of our 3-step process is shown in Figure 6 based on several variations of Ψ. For example, Ψ may be based on deionization of cobalt only (Figure 6a) or total deionization (Figure 6b). These variations of Ψ, both with n = 1, suggest the same value of dimensionless current in only the first pass (I ≃ 5) but suggest different values in the second and third passes (as designated by the colored stars). This difference can be rationalized by the fact that deionization of Co²⁺ (and not of Li⁺ or Cs⁺) is often greatest at low to moderate dimensionless current (Figure 5a). To select the most suitable operating conditions, we compared total (and individual) deionization, WR, and energy density, Ė, for the sequence of passes that maximizes the figure of merit Ψ in Figure 6 (designated by light blue (a), dark red (b), and orange (c) stars). The sequence that maximizes Ŕ in each step, for instance, leads to relatively low WR, but the energy it consumes is also the least. In comparison, the sequence that

\[
f(\hat{E}) = \hat{E}_{\text{lin}} \equiv 1 - \frac{\hat{E}}{\max \hat{E}} \quad \text{(11)}
\]

or nonlinear with respect to \( \hat{E} \)

\[
f(\hat{E}) = \hat{E}_{\text{quad}} \equiv \sqrt{\frac{1 - \hat{E}/\max \hat{E}}{1 - \min \hat{E}/\max \hat{E}}} \quad \text{(12)}
\]

where “min” and “max” operate on the entire array of energy densities in Figure 5c. Although we only considered eqs 10 and 11 in this study, a nonlinear function such as eq 12 could be used to detract from the merit of steps that operate at high power, such that this penalty would become increasingly severe as \( \hat{E} \) approaches max \( \hat{E} \). In any case, all terms in the expression for Ψ (and hence Ψ itself) would range from 0 to 1.

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maximizes $\Psi_{\text{rat}}$ in each step gives $WR = 58\%$, and it maintains almost 99% deionization of $\text{Co}^{2+}$ with little additional demand for energy. This level of water recovery is similar to those achieved by conventional purification technologies, though it can be increased by selecting an alternate sequence in our process. To make a quantitatively motivated selection, more weight is given to WR by setting $n = 2$ and $f(E) = 1$ in our definition of $\Psi$, as shown in Figure 6c. With this modification, the sequence that maximizes $\Psi_{\text{WR}}$ in each step gives $WR = 58\%$. In response, however, consumption of energy increases considerably. It then seems that WR can be improved in return for higher energy consumption (or lower deionization, by repositioning the splitter) depending on the targets set by the operator.

4.4. Process Intensiﬁcation for Lithium Recovery. For all cases shown in Table 2, total deionization is approximately 98%, and deionization of $\text{Co}^{2+}$ is even greater in our 3-step process. Another practical result is the high deionization of $\text{Li}^+$, which is used (as $\text{LiOH}$) in nuclear reactors for corrosion control by alkalizing the process water.39 For this application, $\text{LiOH}$ is isotopically enriched in lithium-7 which does not interfere with nuclear reactions (unlike lithium-6), and it is sometimes used in demineralizers (also known as ion exchangers) to remove radioactive contaminants from the process water.39 Lithium can be selectively captured and recycled in our system (or reused elsewhere) by integrating capacitive deionization (CDI) with intercalation materials55,56 as a second operation following SED. This process intensiﬁcation can in principle be achieved in two steps, as illustrated in Figure 7. In the ﬁrst step, SED is used to concentrate waste in the brine stream, from which $\text{Li}^+$ is selectively captured in the CDI unit by intercalation into an appropriate electrode such as iron phosphate57 ($\text{Fe(III)PO}_4$) or lithium manganese oxide58 ($\text{LiMn}_2\text{O}_4$). During this process, all cations are driven toward the intercalation electrode, but only $\text{Li}^+$ can be inserted into its crystal lattice because $\text{Ca}^+$ is too large and $\text{Co}^{2+}$ will exhibit strong Coulomb repulsion (vacancies in $\text{FePO}_4$ are ﬁtted for small monovalent cations57). Moreover, the anions are inserted into a porous carbon electrode, where they are electrostatically trapped by the applied potential. Fluid leaving the device in this ﬁrst step will therefore be depleted of lithium and its counterion(s). In the second step, the fresh stream produced by SED is passed through the CDI unit. By reversing the direction of electric ﬁeld, lithium and its counterion(s) are released from the electrodes back into solution and are recovered for later use.

ASSOCIATED CONTENT
Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.9b05380.

Representative calibration curve for ICP–MS, current and voltage data, analysis of species selectivity, and conductivity and pH data (PDF)

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