

DeSelenator: A Se-Removal Process for Environmental Decontamination of Wastewaters from Coal-Burning Power Plants

Jeffrey D. Einkauf,* Zhuoyi Zeng, Ziheng Shen, Pimphan Aye Meyer, Dīana Stamberg, Jonathan Willocks, Maggie Gilliland, Michelle Cagley, Sotira Yiaccoumi, Costas Tsouris, and Radu Custelcean*



Cite This: *ACS Environ. Au* 2026, 6, 116–124



Read Online

ACCESS |



Metrics & More



Article Recommendations



Supporting Information

ABSTRACT: Selenium may become a toxic contaminant of freshwater systems when released into the environment through industrial wastewaters from mining, coal-burning power plants, or oil refining. Efficient and cost-effective Se-removal technologies are therefore necessary to reduce Se concentrations in these wastewaters to below the regulatory discharge limits. In this study, we have demonstrated an effective process that removes Se, mostly as selenate anions, from wastewaters generated by coal-burning power plants. This process, dubbed DeSelenator, leverages the high concentration of sulfate relative to selenate in the wastewater and the propensity of these oxyanions to cocrystallize with benzene-bis-iminoguanidinium (BBIG) cations into extremely insoluble salts (on par with BaSO_4). The $\text{SO}_4^{2-}/\text{SeO}_4^{2-}$ cocrystallization with BBIG removes over 90% of S and Se from the wastewater. Following removal of the precipitate by filtration, the filtrate is passed over an anion-exchange resin that further reduces selenium concentration to 5 ppb, the EPA's regulatory limit for freshwater systems. Finally, the effluent is passed over an activated carbon column, which removes 99.8% of the residual BBIG ligand remaining after crystallization, allowing for the safe discharge of the treated water into the environment. The Se-removal process was first optimized in the lab at the bench scale and then tested in the field at the Tennessee Valley Authority's Bull Run coal-burning power plant. A technoeconomic assessment found the cost of water treatment with DeSelenator is on par with that of the active biological method, which is currently considered a state-of-the-art Se-removal technology.

KEYWORDS: iminoguanidines, crystal engineering, oxyanions, selenate, sulfate



INTRODUCTION

Selenium is the 30th most abundant element in earth's crust, found primarily in carbonate and phosphate rocks, volcanic and sedimentary soils, and coal, from which it is redistributed to atmospheric, aquatic, and terrestrial environments through natural and anthropogenic processes (e.g., mining, fossil fuel combustion, oil refining, and agriculture).^{1,2} Although Se is considered an essential element for most living organisms at trace levels (40–400 $\mu\text{g}/\text{day}$ for humans), it becomes toxic at higher concentrations.³ As a result, the United States Environmental Protection Agency (EPA) has set stringent regulatory limits of 50 and 5 $\mu\text{g}/\text{L}$ (or ppb) for drinking water and freshwater systems, respectively.^{4–7} The composition of effluents from coal-fired power plants varies depending on the combustion process, pollution control systems, and coal source. However, arsenic, selenium, and mercury are common contaminants that pose significant environmental and health concerns.^{8,9} Although Se can exist in a wide variety of forms, in industrial wastewaters, it is largely present as selenate (SeO_4^{2-}) and selenite (SeO_3^{2-}) oxyanions.¹⁰ Removing these Se anions from wastewater is a critical problem that presents many technical challenges. Besides the extremely dilute Se concentrations involved, competing anions, such as sulfate, are often present in much higher concentrations in waste-

waters, especially those generated by coal-burning power plants. Furthermore, there may be significant variations in Se levels and forms (i.e., selenate vs selenite) and in the wastewater volumes and flows among various industries and even within the same facility over time.¹¹ Treating these wastewaters requires an effective, flexible, and scalable Se-removal technology that can be deployed on different scales and under various conditions.

Various technologies have been developed for Se removal from wastewaters based on physical, chemical, or biological methods. Physical treatment is based primarily on membrane filtration (e.g., nanofiltration or reverse osmosis).¹² Common chemical methods include ion exchange,¹³ adsorption,¹⁴ and coprecipitation.^{15–17} Alternatively, Se removal via reduction of the oxyanions to elemental Se or iron selenides, either chemically (e.g., using zerovalent iron) or electrochemically

Received: August 25, 2025

Revised: October 31, 2025

Accepted: October 31, 2025

Published: November 6, 2025



(through direct electrochemical reduction or electrocoagulation), has also been explored.^{18,19} Finally, active biological methods (ABMet) involve Se-reducing bacteria to reduce selenite and selenate to colloidal Se nanoparticles, which are then removed by filtration.^{20–22} While all these Se-removal technologies have their advantages and limitations, none of them have been demonstrated at full scale to cost-effectively remove Se to less than 5 ppb from waters associated with all industrial sectors. Notwithstanding, ABMet has been designated by the EPA as the “best available Se-removal technology”.²³

We recently reported a benzene bis-iminoguanidinium (BBIG, Figure 1) ligand that effectively removes selenate

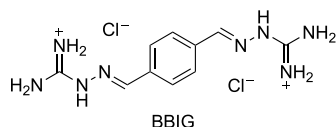


Figure 1. Benzene-bisiminoguanidinium (BBIG) chloride salt used for Se removal from real wastewater by cocrystallization of SO_4^{2-} and SeO_4^{2-} .

from simulated wastewater solutions, even in the presence of excess sulfate, through a crystallization process that leverages the low aqueous solubilities of the corresponding oxyanion salts.^{17,24} X-ray diffraction analysis of the resulting crystals revealed complementary hydrogen bonds between the two guanidinium groups and the O–X–O edges of the oxyanions, leading to extensive hydrogen-bonding networks involving the oxyanions, guanidinium groups, and included water molecules.

Furthermore, the rigid and planar BBIG cations form extended π stacks in these crystals. These structural features lead to the formation of extremely insoluble solids (K_{sp} values in the range of $2.5\text{--}4.4 \times 10^{-10}$), on par with BaSO_4 ($K_{\text{sp}} = 1.1 \times 10^{-10}$).^{25–27} The extremely low solubilities of the crystalline BBIG salts with the two oxyanions and the relatively high concentration of sulfate in the wastewaters ($>10,000\times$ higher than that of selenate) lead to fast precipitation of BBIG–sulfate crystals. Because sulfate and selenate are very similar in size, shape, and charge density, the precipitating BBIG–sulfate crystals include selenate oxyanions that are present in much lower concentrations (<150 ppb) in wastewaters. Up to 99% of Se is thus removed from the simulated wastewaters. Whereas crystallization of the selenate anions with BBIG in the absence of sulfate would enable Se removal down to only the solubility limit of the BBIG–selenate salt (~ 3 ppm (mg/L) Se), cocrystallization with sulfate enables Se removal down to a much lower ppb level. To close the separation cycle, BBIG can be recovered by increasing the solution pH, thereby deprotonating the guanidinium groups, leading to a concentrated alkaline waste stream containing sulfate and selenate oxyanions and recovery of the insoluble neutral BBIG (Figure 2). Finally, BBIG can be converted back into its chloride salt form by treatment with HCl, so it can be recycled. However, while this Se-separation cycle proved effective at the bench scale in the lab under controlled conditions, using simulated wastewater, the Se-removal efficacy from real wastewater under realistic conditions found in the field, as well as the scalability of the process, had yet to be demonstrated.

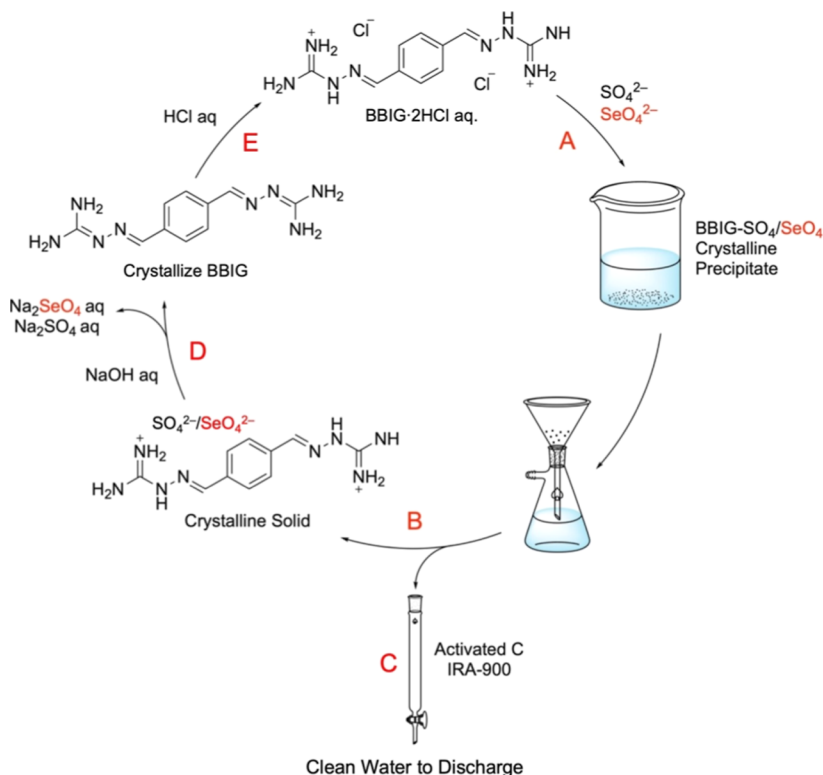


Figure 2. Separation cycle for sulfate/selenate removal by cocrystallization with BBIG. (A) CocrySTALLIZATION of $\text{BBIG}\cdot\text{SO}_4/\text{SeO}_4$. (B) FILTRATION of $\text{BBIG}\cdot\text{SO}_4/\text{SeO}_4$ crystals. (C) TREATMENT of filtrate with ion-exchange resin and activated carbon. (D) BBIG RECOVERY by neutralization with NaOH and crystallization of the neutral ligand; sulfate and selenate are recovered as a concentrated aqueous alkaline solution. (E) REGENERATION of the BBIG chloride salt with dilute HCl.

In this work, we developed and field-tested a Se-removal process at 20 L scale, with real wastewaters collected from the Tennessee Valley Authority's (TVA) Bull Run coal-burning power plant. This study incorporates an activated carbon treatment step to recover residual BBIG, followed by an ion-exchange polishing step to reduce Se concentrations below the 5 ppb EPA limit. The process, called DeSelenator, effectively removes >97% of sulfate and selenate oxyanions through cocrystallization with BBIG. Optimization of the crystallization process was performed to minimize the amount of excess BBIG discharge while still maintaining high selenate crystallization yields. Following crystallization, a post-treatment step was introduced, involving a commercial ion-exchange resin and activated carbon (AC), which further reduced the Se concentration to 5 ppb while removing virtually all remaining BBIG, allowing for the safe discharge of the treated wastewaters. Finally, a technoeconomic analysis (TEA) was conducted on the optimized DeSelenator process to determine the cost drivers and benchmark it against the state-of-the-art ABMet Se-removal technology.

MATERIALS AND METHODS

Materials and Instrumentation

Terephthalaldehyde (>98%, $C_6H_6O_2$) was purchased from Acros Organics; ethanol (95% ACS grade, CH_3CH_2OH) was purchased from Decon Laboratories, Inc.; hydrochloric acid (34–37%, HCl), potassium hydroxide (ACS grade pellets, KOH), and nitric acid (69–70% Optima, HNO_3) were purchased from Fisher Chemical; sodium selenate (BioXtra grade, Na_2SeO_4) and anhydrous sodium sulfate (>99%, Na_2SO_4) were purchased from Sigma-Aldrich; and aminoguanidine hydrochloride (>98%, $CH_6N_4 \cdot HCl$) was purchased from TCI Chemicals. Amberlite IRA-900 anion exchange resin (chloride form) and powder AC were purchased from Sigma-Aldrich. Deionized (DI) H_2O was obtained from a Milli-Q water system operated at 18.2 M Ω cm and 24 °C.

Absorbance spectra were collected on a Shimadzu UV-1900 I UV–vis spectrophotometer using quartz cells with a path length of 0.1 or 1 cm. Absorbance spectra collected at the TVA's Bull Run site were collected using an Ocean Insight dip probe with a path length of 1 cm. The concentration of BBIG·2HCl was determined with Beer's law, using a molar extinction coefficient (ϵ) of $\epsilon_{322\text{ nm}} = 422,173\text{ L mol}^{-1}\text{ cm}^{-1}$.²⁸ Powder X-ray diffraction (PXRD) patterns were collected on a Panalytical Empyrean diffractometer with Ni-filtered Cu K α (1.54 Å) radiation operating at 45 kV and 40 mA. Wide-angle scattering was collected from 5 to 90° for 20 min on a zero-background holder. ICP-MS data were collected on a ThermoScientific iCAP TQ instrument with an Elemental Scientific prepFAST M5 sampling and autodilution system. Aquatic toxicity tests were performed by Environmental Testing Solutions, Inc. Toxicity characteristic leaching protocol experiments were carried out by Eurofins Environment Testing Southeast, LLC.

Sulfate/Selenate Cocrystallization from Leachate Wastewater

In a typical bench-scale experiment, BBIG solid was added to 5 mL of leachate solutions in 15 mL polypropylene centrifuge tubes. Immediately upon addition, a white precipitate formed. The resulting suspensions were mixed for 24 h using a rotator set at 60 rpm inside an incubator set to 25 °C. The samples were then removed and centrifuged for 5 min at 3000 rpm to separate the aqueous and solid phases. A 1 mL aliquot was then removed from each sample and passed through a 0.02 μm syringe filter to ensure any suspended solids were removed from the filtrate prior to diluting the samples in 2% HNO_3 for ICP-MS analysis. The recovered BBIG–oxyanion solid was left to dry for 1 day at room temperature and then analyzed with PXRD. All experiments were performed in triplicate, and the reported concentrations are the average values.

BBIG Regeneration

A volume of 3 mL of DI water was added to the BBIG– SO_4/SeO_4 salt, forming a suspension. KOH (2.1 equiv) was added, or the pH was adjusted to 11 with a KOH solution, and the off-white suspension was mixed for 24 h using a rotator set at 60 rpm inside an incubator at 25 °C. The samples were then passed through a Whatman Autovial syringeless filter device with a 0.45 μm filter. An aliquot of the filtrate was removed for UV–vis and ICP-MS analyses. The recovered neutral BBIG solid was left to dry at room temperature for 1 d and then dissolved in 0.1 M HCl to convert it into the chloride salt. Aliquots were subsequently pulled from the converted BBIG·2HCl salt solution for UV–vis and ICP-MS analyses.

Residual Sulfate/Selenate Removal with IRA-900 Resin

The treated and filtered leachate solution was passed through a fixed-bed ion exchange column using a glass chromatography column (Ace Glass) of 60 cm length and 2.3 cm inner diameter packed with 180 g of IRA-900 resin at a flow rate of 47.5 mL/min for 100 min, corresponding to approximately 5.25 min empty-bed contact time. Liquid samples were collected at various time intervals and analyzed with ICP-MS.

Residual BBIG Removal with Activated Carbon

Following the ion-exchange column treatment, the residual BBIG was removed with AC powder at bench scale. AC of 1 g, 5 g, and 10 g was mixed with 100 mL of distilled water, respectively, in 125 mL flasks for 48 h, at a shaking rate of 90 rpm. Subsequently, the suspension was allowed to settle for 30 min, and liquid samples of 1 mL were collected from the supernatant for UV–vis analysis.

Field Experiments

Wastewater (20 L) was collected from leachate collection systems located beneath a mound of packed fly ash generated by the TVA Bull Run Fossil Plant, an 889 MW coal-fired power station, using a battery-powered pump. ICP-MS survey analysis of the raw wastewater prior to treatment confirmed the presence of multiple elements, including Ca, Mg, Cl, S, Sr, Mn, Li, B, Al, V, Cr, Ni, As, Se, Rb, and Sb. The raw wastewater was transferred into a 10 gal drum after it was passed through a 10 μm mesh-size filter to remove any particulates. BBIG was then added to the clear, colorless wastewater solution, leading to the immediate formation of a white precipitate. The mixture was stirred with an impeller for 1 h, after which it was passed through a filter press (Micronics Engineering Filtration Group Incorporated) to separate the BBIG– SO_4/SeO_4 solid from the supernatant. Solid and solution samples were taken for PXRD, ICP-MS, and UV–vis analyses.

Residual Se and BBIG Removal with Anion-Exchange and Activated Carbon Columns

Following cocrystallization, ion-exchange experiments were conducted using a glass chromatography column (Ace Glass) of 60 cm length and 2.3 cm inner diameter packed with 180 g of IRA-900 resin, followed by a 60 cm long and 2.3 cm inner diameter column packed with 150 g of activated carbon. The filtrate from the filter press was pumped by a Masterflex peristaltic pump at a flow rate of 47.5 mL/min in down-flow mode for 100 min, corresponding to approximately 5.25 min empty-bed contact time. Liquid samples were collected from the outlet of the column at 2.5, 5, 7.5, 10, 12.5, 15, 17.5, 20, 25, 30, 35, 40, 45, 50, 55, 60, 70, 80, 90, and 100 min and analyzed with ICP-MS.

RESULTS AND DISCUSSION

Benchtop Se-Separation Cycles with Real Wastewater

Bench-scale crystallization tests were initially conducted using wastewater collected from the TVA's Bull Run Power Plant site. Variable amounts of BBIG chloride were added, ranging from 1.0 to 1.1 and 2.0 equiv relative to the total S concentration in the wastewater. Previous tests indicated that an excess of BBIG yields the highest removal efficiencies;¹⁷

however, this can also result in excess BBIG left in the water, which must be removed before the effluent waters can be discharged. The initial concentrations of S and Se found in the leachate wastewater were 28.5 ± 0.4 mM (914.8 ± 13.3 ppm of S) and 2.31 ± 0.84 μ M (182.9 ± 6.6 ppb of Se), respectively. When BBIG was added in excess as either 1.1 or 2.0 equiv, the total Se remaining in the leachate was 14.6 ± 1.4 ppb and 12.1 ± 1.2 ppb, respectively (Figure 3). This is nearly

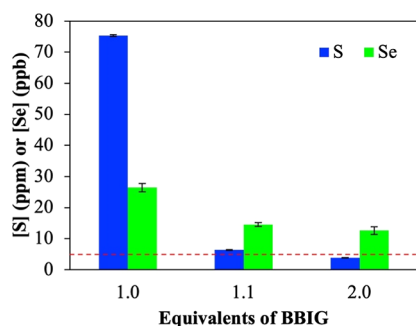


Figure 3. Removal of S (blue, in ppm) and selenium (green, in ppb) from wastewaters collected at the TVA Bull Run site when using various amounts of BBIG chloride. The 5 ppb Se target in the effluent is depicted as a red dashed line.

a 50% reduction in Se concentration compared to 25.6 ± 1.4 ppb remaining Se when 1.0 equiv of BBIG was used. In both cases where BBIG was added in excess, sulfate removal exceeded 99%, while Se removal was slightly lower at about 91%. The lower Se removal efficiency may be attributed to the presence of hydrogen selenite (HSeO_3^- , $\text{p}K_a = 8.1$) in wastewaters ($\text{pH} \sim 7$);²⁹ unlike selenate, selenite does not cocrystallize with sulfate due to its different geometry and charge.¹⁷ Pretreatment of the water with oxidizing agents can convert selenite to selenate; however, any residual oxidant may also oxidize BBIG, and determining the appropriate oxidant dosage in real wastewater systems is challenging. The PXRD pattern of the crystalline solid precipitated from the wastewater matched the expected pattern for the $\text{BBIG} \cdot \text{SO}_4/\text{SeO}_4$ reference solid (Figure S1).

To recover and recycle the BBIG ligand, the $\text{BBIG} \cdot \text{SO}_4/\text{SeO}_4$ crystalline precipitate was treated with aqueous NaOH, adjusting the pH to 11, which resulted in precipitation of BBIG free base and release of sulfate and selenate in the aqueous phase as sodium salts (Table 1). This treatment led to a greater than 96% release of sulfate and selenate into a concentrated waste stream. At the same time, BBIG was converted into its free base form (Figure S2). As the aqueous solubility of BBIG is relatively low ($K_{sp} = 8.4(0) \times 10^{-5}$),¹⁷ more than 90% of the ligand is recovered in the solid form, and the rest remains dissolved in the aqueous waste stream. The concentration factors of S and Se in the effluent stream are 28.9-fold and 27.2-fold, respectively, relative to those of the initial leachate

wastewater. Finally, dissolution of the BBIG free base in 0.1 M HCl regenerates the BBIG chloride salt, thereby closing the separation cycle. The concentration of selenium in the regenerated BBIG chloride solution is 0.70 ± 0.08 ppb, calculated as the average from three independent experiments (Supporting Information, Table S1). The recovery of BBIG relative to the initial $\text{BBIG} \cdot \text{SO}_4/\text{SeO}_4$ crystalline precipitate was in the range of 79–90%.

Se-Separation Cycles with Real Wastewater in the Field

Building on the promising benchtop results, field tests were conducted at TVA's Bull Run coal-burning power plant using 20 L of leachate water collected on the site. In this process, approximately 2.0 equiv of BBIG chloride was added relative to the sulfate concentration, and the mixture was mechanically stirred for 1 h. The 2-fold excess of BBIG was employed to maximize the Se removal efficiency from the leachate water. The resulting slurry was subsequently suctioned into a filter press to separate the $\text{BBIG} \cdot \text{SO}_4/\text{SeO}_4$ solid from the treated wastewater, and its identity was confirmed by PXRD (Figure S3). ICP-MS analysis of the filtered solution showed effective reduction of S concentration from 921.8 ± 15.3 ppm to 8.3 ± 1.1 ppm, corresponding to a S removal efficiency of 99.1% (Table 2). At the same time, Se concentration was reduced from 173.1 ± 4.9 ppb to 12.8 ± 2.8 ppb, corresponding to a Se removal efficiency of 92.6%.

Suspending the crystalline $\text{BBIG} \cdot \text{SO}_4/\text{SeO}_4$ solid in an aqueous NaOH solution with a pH of about 11 led to crystallization of the BBIG free base and a near quantitative release of sulfate and selenate in the solution as concentrated sodium salts (Table S2). More than 96% of both sulfate and selenate were released from the crystalline precipitate into the concentrated alkaline waste stream, resulting in a 28.9-fold and 27.1-fold increase in S and Se concentrations, respectively, relative to the untreated leachate water. At the same time, 97.1% of BBIG was recovered as solid BBIG (Figure S4 and Table S2), while the residual BBIG concentration in the filtrate was 35.1 μ M. The subsequent dissolution of the BBIG free base with 0.1 M HCl regenerated the BBIG dichloride salt. The final concentrations of S and Se in the acidic solution (Table S3) indicate the essentially quantitative release of the two oxyanions from the crystalline $\text{BBIG} \cdot \text{SO}_4/\text{SeO}_4$ solid by this treatment. Overall, through the complete recovery process, encompassing both basic and acidic pH swings, $90.7 \pm 2.1\%$ of BBIG was recovered relative to the initial $\text{BBIG} \cdot \text{SO}_4/\text{SeO}_4$ solid (Table S4).

While the cocrystallization step with BBIG removed the bulk of the sulfate and selenate anions from the leachate water, the concentration of Se in the filtrate, of about 13 ppb, was still above the optimal value of 5 ppb recommended by the EPA. To further reduce the Se concentration, a second treatment step involving an anion-exchange column was added to the process. It is important to mention here that the anion-exchange column on its own, without prior bulk removal of

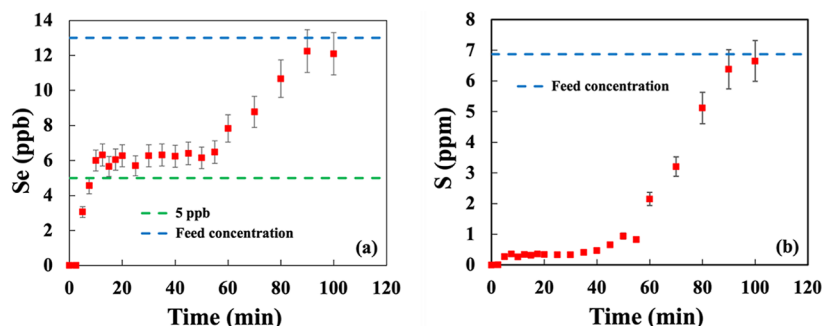
Table 1. Sulfate and Selenate Release and BBIG Recovery Efficiencies after Treatment of the $\text{BBIG} \cdot \text{SO}_4/\text{SeO}_4$ Crystalline Solid with NaOH

[BBIG]/[S]	[S] (mM)	%S release ^a	[Se] (μ M)	%Se release ^a	% BBIG recovery ^a
1.0	814.6 ± 2.2	99.2 ± 0.6	60.2 ± 0.3	96.8 ± 0.9	98.4 ± 0.3
1.1	826.9 ± 4.1	96.9 ± 1.2	63.3 ± 0.6	97.1 ± 0.4	98.5 ± 0.2
2.0	837.4 ± 4.4	98.0 ± 2.1	65.1 ± 0.5	97.8 ± 1.8	98.4 ± 0.3

^aValues are relative to the initial BBIG–oxyanion precipitate.

Table 2. BBIG and Oxyanion Concentrations and Oxyanion Removal Efficiencies of the First Precipitation Step in the Sulfate/Selenate Separation in the Field Using 20 L of Leachate

sample	[S] (ppm)	[S] (mM)	[Se] (ppb)	[Se] (μ M)	%S removal	%Se removal	%S/%Se
untreated	921.8 $\pm$ 15.3	28.7 $\pm$ 0.01	173.1 $\pm$ 4.9	2.2 $\pm$ 0.1			
treated	8.3 $\pm$ 1.1	0.25 $\pm$ 0.03	12.8 $\pm$ 2.8	0.2 $\pm$ 0.1	99.1	92.6	1.07

**Figure 4.** Breakthrough profiles for Se (a) and S (b) with the influent of leachate wastewater after precipitation with BBIG. The influent concentrations of S and Se are represented by a blue dashed line. The target EPA regulatory limit of 5 ppb is depicted as a green dashed line.

sulfate and selenate anions, is inadequate for removal of trace amounts of Se (i.e., ppb concentration) in the presence of such a large excess of competing sulfate. Unlike the treatment with BBIG, where the $\text{SO}_4^{2-}/\text{SeO}_4^{2-}$ cocrystallization is cooperative (i.e., sulfate crystallization facilitates selenate removal by its inclusion in the growing sulfate crystals), an anion-exchange resin becomes quickly saturated with sulfate, resulting in fast Se breakthrough.

Passing the filtrate solution resulting from cocrystallization through an ion-exchange column containing 180 g of IRA-900 resin led to a first Se breakthrough at around 10 min, with the Se concentration in the effluent remaining stable around 6 ppb until 60 min (Figure 4a). At 60 min, a second Se breakthrough was observed, and the Se concentration in the effluent increased steadily until it reached the feed solution concentration, indicating saturation of the resin. The first Se breakthrough observed at around 10 min can be attributed to selenite breakthrough. This is due to the lower selectivity of IRA-900 for selenite over that of selenate. Another observation supporting this explanation is that only one breakthrough for S was observed at the same time the second selenium breakthrough occurred, due to the resin saturation with SO_4^{2-} (Figure 4b). These observations suggest that the resin has similar affinities for SO_4^{2-} and SeO_4^{2-} . Thus, the IRA-900 resin efficiently removes the residual Se from the leachate water, following cocrystallization of bulk SO_4^{2-} and SeO_4^{2-} with BBIG.

While an effluent selenium concentration at or below 5 ppb was not maintained throughout this experiment, the results provide clear evidence of the feasibility and effectiveness of the IRA-900 anion-exchange process. Achieving sustained concentrations at or below 5 ppb is expected to be achieved through conventional column optimization strategies, including reducing the flow rate and increasing the bed depth and resin mass. In addition, in practical applications involving mixed effluent streams, an average concentration of 5 ppb can still be achieved, even if some individual sampling points exceed this value.

Reducing the Amount of BBIG in the Filtrate

The preliminary tests described in the previous sections indicated that an excess of the BBIG ligand is necessary to

achieve high Se removal efficiencies from real wastewaters. However, excess BBIG ligand discharged with the treated wastewater may be harmful to aquatic life. To assess its toxicity, BBIG-2HCl was screened against water fleas (*Ceriodaphnia dubia*) and fathead minnow larvae (*Pimephales promelas*). The results listed in Table 3 indicate that this

Table 3. Aquatic Toxicity (LC_{50}) Results of the BBIG Chloride Salt Assessed by Screening Tests against Water Fleas (*C. dubia*) and Fathead Minnow Larvae (*P. promelas*)

organism	time (h)	toxicity (mg/L)	toxicity (μ M)
water flea	24	3.31	9.32
	48	1.67	4.70
minnow larvae	24	15.7	44.20
	48	14.7	41.38
	72	13.8	38.85
	96	13.5	38.00

organic ligand is toxic to aquatic species at concentrations above 4.70 μ M (1.67 ppm). Thus, the residual BBIG needs to be removed from the treated water prior to its discharge into the environment.

To mitigate the contamination of the treated water with BBIG, we first looked to minimize the amount of BBIG used in the crystallization step while maintaining high Se-removal efficiency. Toward this goal, we fine-tuned the amount of BBIG added by exploring a range from 0.950 to 1.050 mol equiv relative to sulfate content in the wastewater (Table S5). As expected, as the BBIG concentration increased, more Se was removed from the solution; at the same time, a higher amount of unreacted BBIG remained in the filtrate. Based on these results, we decided to proceed with 0.950 mol equiv of BBIG relative to sulfate, resulting in a residual BBIG concentration of 7.71 μ M in the treated water after crystallization and filtration, which is near the target LC_{50} value of 4.70 μ M. At the same time, Se concentration after crystallization was reduced to 12.08 ppb. The remaining BBIG was removed by adsorption with activated carbon. Screening experiments indicated that the concentration of BBIG in an aqueous solution can be reduced from 35.1 μ M BBIG to 0.272 μ M (Figures S5 and S6) after just 1 min of contact time with

Table 4. BBIG and Oxyanion Concentrations and Oxyanion Removal Efficiencies for the Cocrystallization and Column Steps Involving 0.950 equiv BBIG and 5 L of Leachate Water

sample	[S] (ppm)	[S] (mM)	[Se] (ppb)	[Se] (μ M)	%S removal ^a	%Se removal ^a	%S/%Se
untreated	1041.6 $\pm$ 20.3	32.5 $\pm$ 0.6	195.7 $\pm$ 8.7	2.5 $\pm$ 0.1			
treated	133.1 $\pm$ 16.9	4.2 $\pm$ 0.9	18.8 $\pm$ 3.5	0.2 $\pm$ 0.03	87.2 $\pm$ 2.3	90.4 $\pm$ 3.4	0.98
after column	50.9 $\pm$ 10.2	1.6 $\pm$ 0.3	5.7 $\pm$ 0.8	0.1 $\pm$ 0.01	95.1 $\pm$ 5.8	97.1 $\pm$ 6.6	0.98

^aValues are relative to the initial, untreated solution.

activated carbon. This corresponds to a removal efficiency of 99.2% (Table S6). Extending the contact time to 30 min, the BBIG concentration decreased further to 0.073 μ M, achieving a BBIG removal efficiency of 99.8%. Thus, by minimizing the amount of BBIG used for crystallization and subsequently treating the solution with activated carbon, we can successfully lower the residual BBIG concentration below the aquatic toxicity threshold while maintaining high Se-removal efficiency.

Fully Optimized Se-Removal Cycle

Having optimized the conditions for the effective removal of both Se and residual BBIG, we returned to the TVA's Bull Run site for a final field test of DeSelenator, using 5 L of leachate water. Upon adding 0.95 mol equiv of BBIG to the wastewater, removal of 87.2 $\pm$ 2.3% S and 90.4 $\pm$ 3.4% Se from solution was achieved by cocrystallization (Table 4). The treated solution was subsequently passed through an activated carbon-packed column, lowering the residual BBIG concentration from 6.98 to 0.5 μ M (Figure S7), and then through an IRA-900 resin-packed column, which further reduced the Se concentration to 5.7 $\pm$ 0.8 ppb. Thus, the concentrations of both Se and BBIG in the final treated water are below the corresponding aquatic toxicity limits, rendering it safe for environmental discharge.

Finally, the recovered BBIG–oxyanion solid from the optimized treatment cycle was brought back to the lab for BBIG regeneration by treatment with NaOH. The filtered concentrated basic waste stream (pH 11) contained 826.1 $\pm$ 0.6 mM S and 64.1 $\pm$ 0.2 μ M Se, representing a 25-fold increase in concentration compared to the initial wastewater (Table 5). The insoluble BBIG free base was then treated with

Table 5. Efficiencies of Sulfate and Selenate Release during the Regeneration of BBIG with Aqueous NaOH

[S] (mM)	%S release ^a	[Se] (μ M)	%Se release ^a
826.1 $\pm$ 0.6	96.8 $\pm$ 0.3	64.1 $\pm$ 0.2	97.2 $\pm$ 0.7

^aValues are relative to the initial BBIG·SO₄/SeO₄ precipitate.

an acidic HCl solution to regenerate the starting BBIG·HCl salt. The final concentrations of S and Se in the acidic solution were found to be below the ICP-MS detection limit. Throughout this process, 79.8 $\pm$ 4.9% of BBIG was successfully recovered from the initial BBIG·SO₄/SeO₄ solid.

Technoeconomic Analysis

A TEA was conducted to evaluate the process economics, identify process cost drivers, and suggest opportunities for improvements toward a competitive Se-removal technology. The TEA, developed in ASPEN Plus software,³⁰ was based on the process block flow diagram shown in Figure 5, at a scale of 163,530 L of treated water per day (30 gal min^{−1}). The experimental results obtained from the field tests at the TVA's Bull Run plant were used for this analysis. Wastewater is co-fed with BBIG·2HCl solution to a crystallization unit where BBIG·

SO₄/SeO₄ solid precipitates. A filtration unit is subsequently applied to remove BBIG·SO₄/SeO₄ from the water. An ion exchange column followed by an activated carbon column was then used to further remove selenium to a concentration of 5 ppb Se and remove residual BBIG, respectively. The BBIG material is recovered by treatment of the BBIG·SO₄/SeO₄ solid with an ammonium hydroxide base solution to generate concentrated solutions of ammonium sulfate and selenate and solid BBIG, which can be separated out from the solution by a centrifuge. The recovered BBIG is converted on-site into the chloride salt by treatment with a hydrochloric acid solution. A BBIG recovery efficiency of 90.7% was considered in this analysis based on the experimental data.

For this TEA, each piece of equipment and unit operation was sized and then costed by using the Aspen Process Economic Analyzer tool.³¹ Electricity is required to operate pumps, filtration units, mixing tanks, solid feeders, and centrifuges, and the consumption was estimated either using the simulation tool or calculated based on a previous process design report case study.³² Operating cost components include raw material, utility, maintenance material, and labor, while capital cost components include plant overhead, tax, insurance, and capital depreciation. Financial assumptions and chemical costs were taken from the process economics analysis and database in the Process Economics Program by S&P Global.³³

ABMET, designated as EPA's best available technology (BAT) for selenium removal to concentrations below 5 ppb, has been used as a benchmark. Capital and operating cost curves of ABMET are published elsewhere.²³ Our TEA results suggest the process economics of DeSelenator are comparable to those of the ABMET process at \$16 per 1000 L of treated water. The analysis summary in Figure 6 shows that ABMET is a capital-intensive process, while DeSelenator is more operating cost intensive. Thus, the capital cost of ABMET is more than four times larger than the capital cost of DeSelenator (MM\$10.5 vs MM\$2.4 installed equipment). On the other hand, the annual operating cost of DeSelenator is approximately 30% higher compared to ABMET (MM\$0.8 per year vs MM\$0.5 per year). The most significant operating cost driver for the DeSelenator process is raw material/chemical cost (71% of the total cost) including makeup BBIG (\$2/1000 L or 16% of the total raw material cost) and chemicals for BBIG material regeneration steps (\$10/1000 L or 84% of the total raw material cost). Accordingly, improvement and optimization of the BBIG regeneration step has the highest potential for lowering the cost of this novel Se-removal technology. On the other hand, the much lower capital cost of DeSelenator will require much less time for the return of investment, thereby adding significant flexibility. Another advantage of DeSelenator is that the process can be designed as a mobile unit placed as needed by conventional wastewater treatment trains, which are typically operated without a selenium treatment unit. Additional flexibility comes from the option to leave the removed Se in the solid form, as a

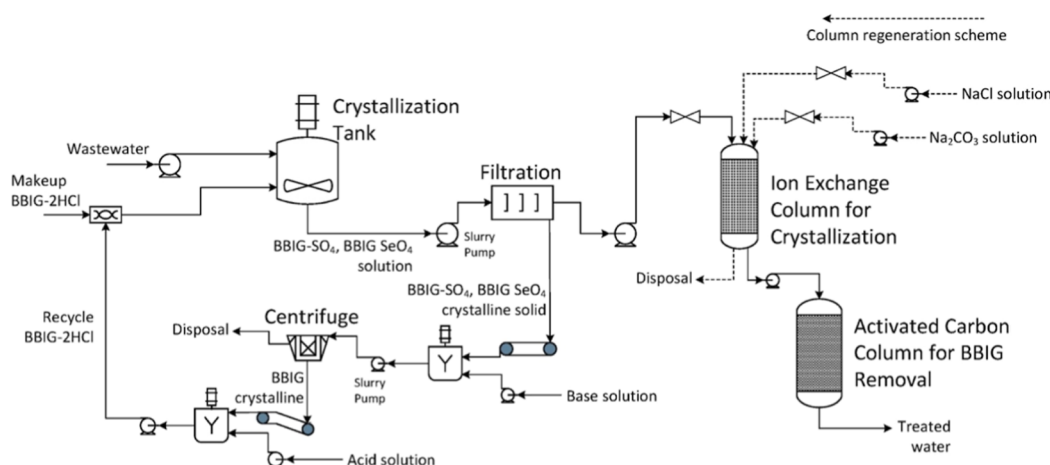


Figure 5. Process diagram of using BBIG-2HCl to remove sulfur and selenium from wastewater. The wastewater treatment cost is presented and compared to that of an existing technology in Figure 6.

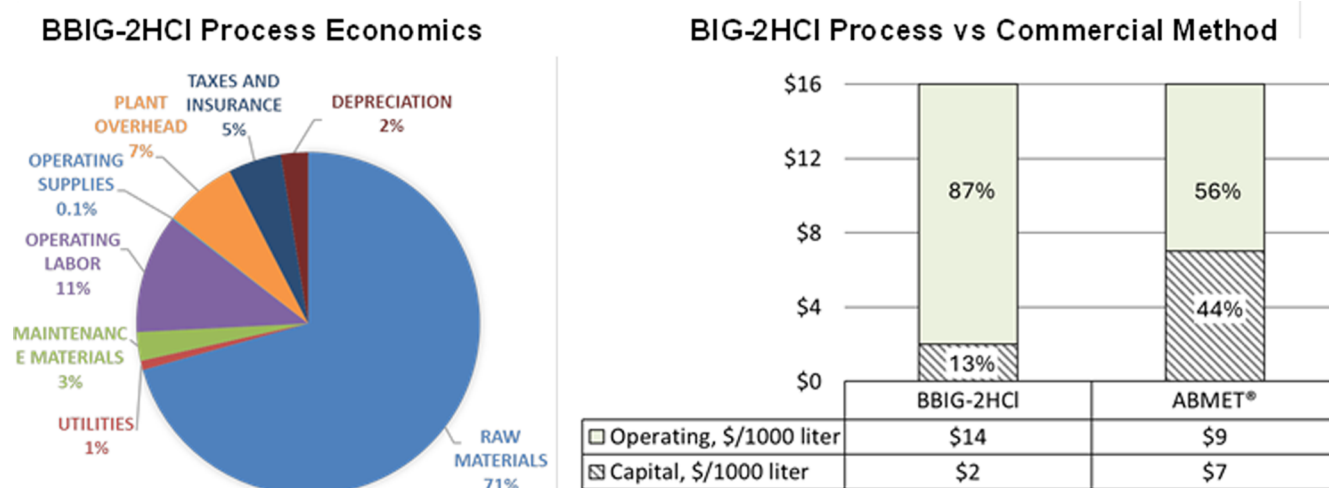


Figure 6. Cost analysis (in 2020\$ cost year) of the DeSelenator process and benchmarking against the ABMET commercial process.

mixed BBIG–sulfate/selenate salt. A toxicity characteristic leaching procedure conducted on the BBIG- SO_4/SeO_4 solid (Table S7) showed virtually no Se leaching into the soil under conditions that simulate landfill storage. This offers the option of manifesting the removed Se as a nontoxic waste through simple landfill disposal, although at a higher overall cost to compensate for the expense of fresh BBIG manufacturing (Supporting Information).

CONCLUSIONS

A Se-removal process (DeSelenator) for the decontamination of leachate waters from coal-burning power plants was demonstrated. DeSelenator offers an effective, low-maintenance, flexible, and easily scalable technology that removes highly toxic Se from wastewaters. The technology combines simple crystallization and ion-exchange column processes that have been field-tested with real wastewater at TVA's Bull Run power plant. The final Se concentration of the treated water is at 5 ppb, the EPA set limit, and the removed Se can be simply manifested in the landfill as nontoxic solid waste. The cost of water treatment with DeSelenator is on par with that of the active biological method, which is state-of-the-art Se-removal technology. Furthermore, the DeSelenator has a much lower

capital cost and provides increased mobility and flexibility. Overall, this work offers an efficient, field-deployable, and cost-effective technology for the removal of trace amounts of toxic Se from wastewaters to meet safe discharge limits.

ASSOCIATED CONTENT

Data Availability Statement

Data will be made available on request.

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsenvironau.5c00190>.

Experimental procedures, material characterization data, TCLP data, and TEA data (PDF)

AUTHOR INFORMATION

Corresponding Authors

Jeffrey D. Einkauf – Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States; orcid.org/0000-0002-6403-4301; Email: einkaufjd@ornl.gov

Radu Custelcean – Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States

States; orcid.org/0000-0002-0727-7972;
Email: custelceanr@ornl.gov

Authors

- Zhuoyi Zeng** – School of Civil and Environmental Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, United States
- Ziheng Shen** – School of Civil and Environmental Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, United States; orcid.org/0000-0001-6429-5897
- Pimphan Aye Meyer** – Manufacturing Science Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States
- Diāna Stamberg** – Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States; orcid.org/0000-0002-6336-3402
- Jonathan Willocks** – Manufacturing Science Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States
- Maggie Gilliland** – Tennessee Valley Authority, Chattanooga, Tennessee 37402, United States
- Michelle Cagley** – Tennessee Valley Authority, Chattanooga, Tennessee 37402, United States
- Sotira Yiaccoumi** – School of Civil and Environmental Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, United States; orcid.org/0009-0003-5827-6050
- Costas Tsouris** – School of Civil and Environmental Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, United States; Manufacturing Science Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States; orcid.org/0000-0002-0522-1027

Complete contact information is available at:
<https://pubs.acs.org/10.1021/acsenvironau.5c00190>

Author Contributions

Jeffrey D. Einkauf: Formal Analysis, Investigation, Methodology, Writing—original Draft. **Zhuoyi Zeng:** Investigation, Writing—review and editing. **Ziheng Shen:** Investigation, Writing—review and editing. **Pimphan Aye Meyer:** TEA. **Diāna Stamberg:** Methodology. **Jonathan Willocks:** Methodology. **Maggie Gilliland:** Resources, Validation. **Michelle Cagley:** Resources, Validation. **Sotira Yiaccoumi:** Methodology, Investigation, Resources, Writing—review and editing, Supervision. **Costas Tsouris:** Methodology, Investigation, Resources, Writing—review and editing. **Radu Custelcean:** Conceptualization, Funding acquisition, Writing—review and editing, Supervision.

Notes

This manuscript has been authored by UT-Battelle, LLC under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy. The United States Government retains and the publisher, by accepting the article for publication, acknowledges that the United States Government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes. The Department of Energy will provide public access to these results of federally sponsored research in accordance

with the DOE Public Access Plan (<http://energy.gov/downloads/doe-public-access-plan>).
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This manuscript was supported by the National Alliance for Water Innovation (NAWI) through funding from the U.S. Department of Energy (DOE), Office of Energy Efficiency and Renewable Energy, Advanced Manufacturing Office under Funding Opportunity Announcement DE-FOA-0001905.

REFERENCES

- (1) Gebreyesus, G. D.; Zewge, F. A review on environmental selenium issues. *SN Appl. Sci.* **2019**, *1* (1), 55.
- (2) Guo, K.; Li, Y.; Wang, J.; Sui, Z.; Wang, T.; Pan, W.-P. A review on selenium in coal-fired power plants: Content and forms in coal, determination methods, migration, transformation, and control technologies. *J. Environ. Chem. Eng.* **2024**, *12* (5), 113579.
- (3) Tan, L. C.; Nanchaiah, Y. V.; van Hullebusch, E. D.; Lens, P. N. L. Selenium: environmental significance, pollution, and biological treatment technologies. *Biotechnol. Adv.* **2016**, *34* (5), 886–907.
- (4) *Technical Support for Adopting and Implementing the EPA's 2016 Selenium Criterion in Water Quality Standards*; EPA 820-R-24-001; United States Environmental Protection Agency, 2024.
- (5) *Proposed Selenium Criterion Maximum Concentration for the Water Quality Guidance for the Great Lakes System*; 40 CFR 132; Environmental Protection Agency, 1996.
- (6) *Protection of Environment: Water Programs*; 40 CFR 132; Environmental Protection Agency, 2025.
- (7) Abidli, A.; Huang, Y.; Ben Rejeb, Z.; Zaoui, A.; Park, C. B. Sustainable and efficient technologies for removal and recovery of toxic and valuable metals from wastewater: Recent progress, challenges, and future perspectives. *Chemosphere* **2022**, *292*, 133102.
- (8) Ruhl, L.; Vengosh, A.; Dwyer, G. S.; Hsu-Kim, H.; Schwartz, G.; Romanski, A.; Smith, S. D. The Impact of Coal Combustion Residue Effluent on Water Resources: A North Carolina Example. *Environ. Sci. Technol.* **2012**, *46* (21), 12226–12233.
- (9) Yao, Z.; Kim, D.; Bravo, J.; Romero, C.; Oztekin, A.; Norris, P.; Cohron, M.; Baltrusaitis, J. Experimental Characterization and Quantification of Effluent Contaminants in Wastewater Streams from Coal-Fired Power Plants. *ACS ES&T Water* **2024**, *4* (6), 2458–2469.
- (10) Lenz, M.; Lens, P. N. The essential toxin: the changing perception of selenium in environmental sciences. *Sci. Total Environ.* **2009**, *407* (12), 3620–3633.
- (11) Bailey, R. T. Review: Selenium contamination, fate, and reactive transport in groundwater in relation to human health. *Hydrogeol. J.* **2017**, *25* (4), 1191–1217.
- (12) Boussouga, Y.-A.; Than, H.; Schäfer, A. I. Selenium species removal by nanofiltration: Determination of retention mechanisms. *Sci. Total Environ.* **2022**, *829*, 154287.
- (13) Gezer, N.; Gülfen, M.; Aydın, A. O. Adsorption of selenite and selenate ions onto thiourea-formaldehyde resin. *J. Appl. Polym. Sci.* **2011**, *122* (2), 1134–1141.
- (14) Opiso, E.; Sato, T.; Yoneda, T. Adsorption and co-precipitation behavior of arsenate, chromate, selenate and boric acid with synthetic allophane-like materials. *J. Hazard. Mater.* **2009**, *170* (1), 79–86.
- (15) Tokunaga, K.; Takahashi, Y. Effective Removal of Selenite and Selenate Ions from Aqueous Solution by Barite. *Environ. Sci. Technol.* **2017**, *51* (16), 9194–9201.
- (16) Prieto, M.; Astilleros, J. M.; Fernández-Díaz, L. Environmental Remediation by Crystallization of Solid Solutions. *Elements* **2013**, *9* (3), 195–201.
- (17) Einkauf, J. D.; Williams, N. J.; Seipp, C. A.; Custelcean, R. Near Quantitative Removal of Selenate and Sulfate Anions from Wastewaters by Cocrystallization with Chelating Hydrogen-Bonding Guanidinium Ligands. *JACS Au* **2023**, *3* (3), 879–888.

(18) Zou, S.; Mauter, M. S. Direct Electrochemical Pathways for Selenium Reduction in Aqueous Solutions. *ACS Sustainable Chem. Eng.* **2021**, 9 (5), 2027–2036.

(19) Yuan, Y.; Mehrotra, M.; He, X.; Flynn, E. D.; Catalano, J. G.; Giammar, D. E. Advancing Selenium(VI) Removal by Iron Electrocoagulation: Roles of Water Chemistry and Operating Conditions. *ACS ES&T Eng.* **2025**, 5 (7), 1821–1830.

(20) Sinharoy, A.; Saikia, S.; Pakshirajan, K. Biological removal of selenite from wastewater and recovery as selenium nanoparticles using inverse fluidized bed bioreactor. *J. Water Proc. Eng.* **2019**, 32, 100988.

(21) Sinharoy, A.; Lens, P. N. L. Biological Removal of Selenate and Selenite from Wastewater: Options for Selenium Recovery as Nanoparticles. *Curr. Pollut. Rep.* **2020**, 6 (3), 230–249.

(22) Eswayah, A. S.; Smith, T. J.; Gardiner, P. H. E. Microbial Transformations of Selenium Species of Relevance to Bioremediation. *Appl. Environ. Microbiol.* **2016**, 82 (16), 4848–4859.

(23) NAMC White Paper Report Addendum. <https://www.namc.org/docs/00113597.pdf> (accessed 2025 July 15).

(24) Custelcean, R. Iminoguanidines: from anion recognition and separation to carbon capture. *Chem. Commun.* **2020**, 56 (71), 10272–10280.

(25) Custelcean, R.; Williams, N. J.; Seipp, C. A. Aqueous Sulfate Separation by Crystallization of Sulfate-Water Clusters. *Angew. Chem., Int. Ed.* **2015**, 54 (36), 10525–10529.

(26) Williams, N. J.; Seipp, C. A.; Brethomé, F. M.; Ma, Y.-Z.; Ivanov, A. S.; Bryantsev, V. S.; Kidder, M. K.; Martin, H. J.; Holguin, E.; Garrabrant, K. A.; et al. CO₂ Capture via Crystalline Hydrogen-Bonded Bicarbonate Dimers. *Chem* **2019**, 5 (3), 719–730.

(27) Djamali, E.; Chapman, W. G.; Cox, K. R. A Systematic Investigation of the Thermodynamic Properties of Aqueous Barium Sulfate up to High Temperatures and High Pressures. *J. Chem. Eng. Data* **2016**, 61 (10), 3585–3594.

(28) Custelcean, R.; Williams, N. J.; Seipp, C. A.; Ivanov, A. S.; Bryantsev, V. S. Aqueous Sulfate Separation by Sequestration of [(SO₄)₂(H₂O)₄]^{4−} Clusters within Highly Insoluble Imine-Linked Bis-Guanidinium Crystals. *Chem.—Eur. J.* **2016**, 22 (6), 1997–2003.

(29) Paydary, P.; Schellenger, A. E. P.; Teli, M.; Jaisi, D. P.; Onnis-Hayden, A.; Larese-Casanova, P. Chemical oxidation of selenite to selenate: Evaluation of reactive oxygen species and O transfer pathways. *Chem. Geol.* **2021**, 575, 120229.

(30) AspenTech Aspen Plus, Process model and optimization software. <https://www.aspentech.com/en/products/engineering/aspen-plus> (accessed September 2025).

(31) Aspen Process Economic Analyzer. <https://www.aspentech.com/en/products/engineering/aspen-process-economic-analyzer> (accessed June 2025).

(32) Humbird, D.; Davis, R.; Tao, L.; Kinchin, C.; Hsu, D.; Aden, A.; Schoen, P.; Lukas, J.; Olthof, B.; Worley, M.; et al. *Process Design and Economics for Biochemical Conversion of Lignocellulosic Biomass to Ethanol: Dilute-Acid Pretreatment and Enzymatic Hydrolysis of Corn Stover*; NREL/TP-5100–47764; TRN: US201110%638; National Renewable Energy Lab. (NREL), Golden, CO (United States), United States, 2011. <https://www.osti.gov/biblio/1013269>, <https://www.osti.gov/servlets/purl/1013269>.

(33) Global, S. P. Process Economics Program. <https://www.spglobal.com/commodity-insights/en/products-solutions/chemicals/chemical-process-economics-program-pep> (accessed June 2025).



CAS INSIGHTS™

EXPLORE THE INNOVATIONS SHAPING TOMORROW

Discover the latest scientific research and trends with CAS Insights. Subscribe for email updates on new articles, reports, and webinars at the intersection of science and innovation.

Subscribe today

CAS
A division of the American Chemical Society