

-Supporting Information-

Tunable Production of Elemental Se vs H₂Se Through Photocatalytic Reduction of Selenate in Synthetic Mine Impacted Brine: Engineering a Recoverable Se Product

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Table S1. Treatability results from SMIB A, B and C including the apparent first-order reaction rate constant and the average selectivity to $\text{Se}^0_{(s)}$ for the photocatalytic reduction of selenate in synthetic brine under reaction conditions of 0.2 g L⁻¹ TiO₂, pH 4.5, 300 mg L⁻¹ formic acid and 37°C.

Parameter	Units	SMIB A		SMIB B		SMIB C	
		Raw	Treated (2.1x10 ²⁰ photons cm ⁻²)	Raw	Treated (2.1x10 ²⁰ photons cm ⁻²)	Raw	Treated (2.1x10 ²⁰ photons cm ⁻²)
Photocatalytic Kinetic Data							
$k_{\text{app},1}$	cm ² /10 ²⁰ photons		1.299 ± 0.043		1.206 ± 0.046		2.139 ± 0.066
Average selectivity to $\text{Se}^0_{(s)}$	-		0.468		0.311		0.328
Physical Tests (Water)							
Total Dissolved Solids	mg/L	6250	5700	5900	5730	5810	5670
Hardness (as CaCO ₃)	mg/L	2120	2130	2030	2020	1930	1920
pH	pH	8.16	4.89	7.81	5.2	7.54	4.94
ORP	mV	390	291	377	332	387	242
Anions and Nutrients (Water)							
Alkalinity, Total (as CaCO ₃)	mg/L	200	22.1	34	28.9	19.7	18.8
Ammonia (as N)	mg/L	0.0429	1.36	0.0265	1.41	0.0246	2.38
Nitrate (as N)	mg/L	556	528	546	528	535	510
Nitrite (as N)	mg/L	<0.0050	0.142	<0.0050	0.154	<0.0050	0.157
Chloride (Cl)	mg/L	58.8	135	58.7	126	799	846
Sulfate (SO ₄)	mg/L	1720	1680	1700	1680	723	690
Organic / Inorganic Carbon (Water)							
Total Inorganic Carbon	mg/L	39.3	<0.50	3.64	<0.50	2.4	<0.50
Total Organic Carbon	mg/L	1.92	67.8	1.8	68	1.35	64.5
Total Metals (Water)							
Calcium (Ca)-Total	mg/L	485	480	454	459	418	410
Magnesium (Mg)-Total	mg/L	235	226	221	215	230	218
Selenium (Se)-Total	ug/L	3280	165	3350	191	2720	32
Sodium (Na)-Total	mg/L	826	863	859	971	865	947
Titanium (Ti)-Total	mg/L	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010

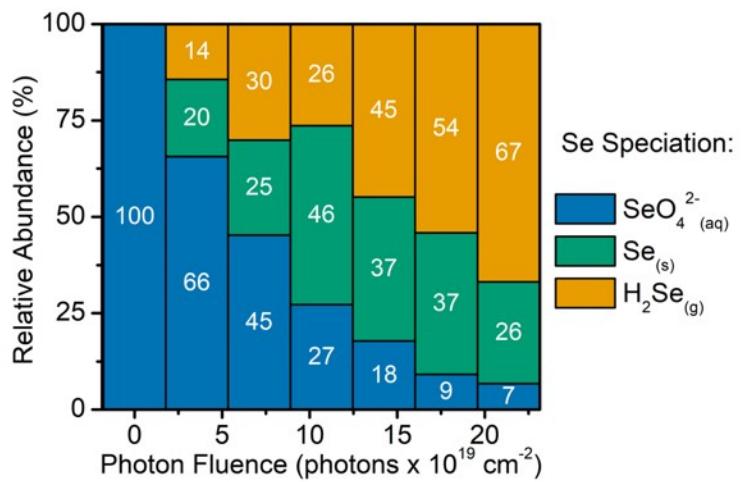


Figure S1. Relative Se speciation during photocatalytic reduction of selenate in SMIB A under 37°C, 300 mg/L formic acid, 0.5 g/L TiO₂, pH 4.5 reaction conditions.

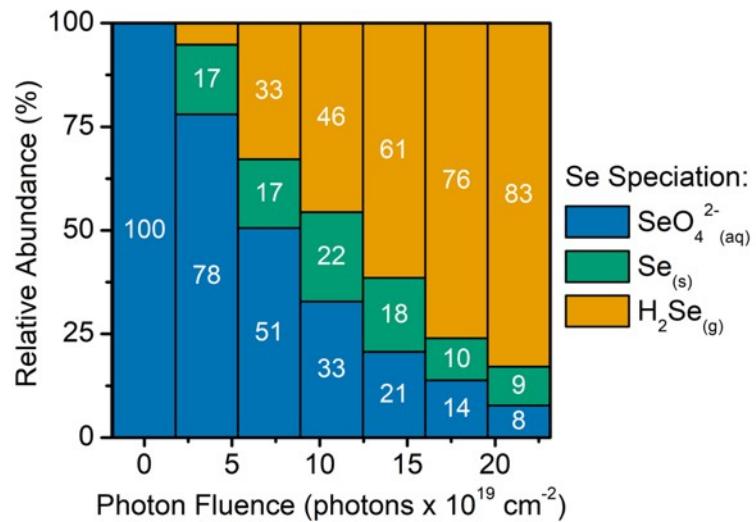


Figure S2. Relative Se speciation during photocatalytic reduction of selenate in SMIB B under 37°C, 300 mg/L formic acid, 0.5 g/L TiO₂, pH 4.5 reaction conditions.

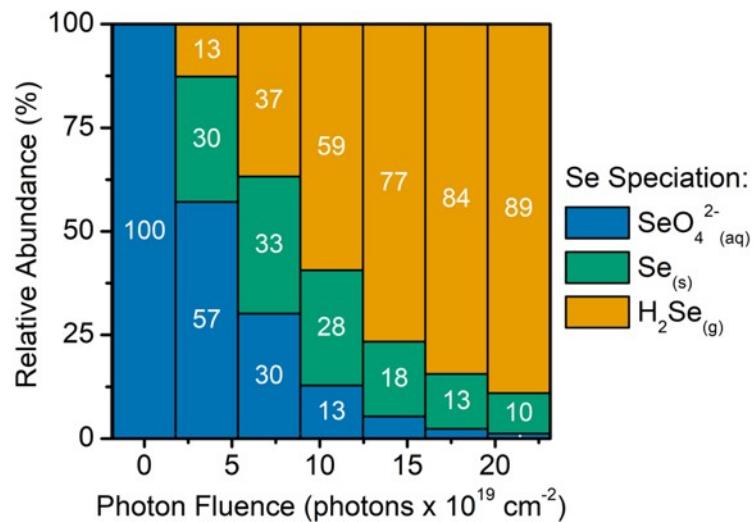


Figure S3. Relative Se speciation during photocatalytic reduction of selenate in SMIB C under 37°C, 300 mg/L formic acid, 0.5 g/L TiO₂, pH 4.5 reaction conditions.

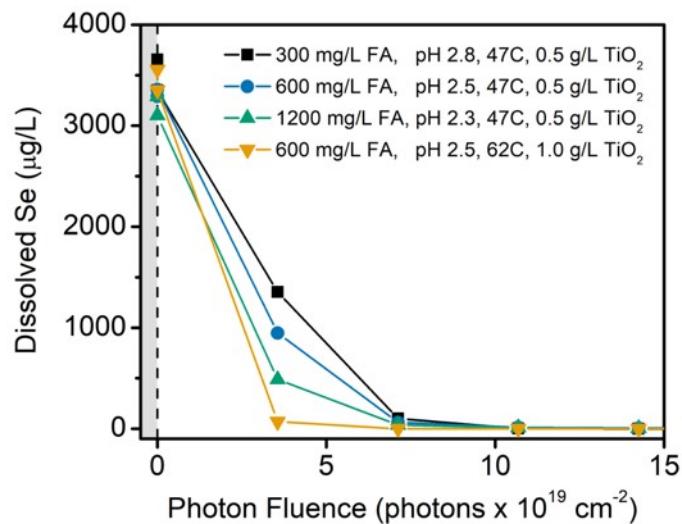


Figure S4. Selenate removal curves through the photocatalytic reduction of selenate in SMIB at varying reaction conditions.

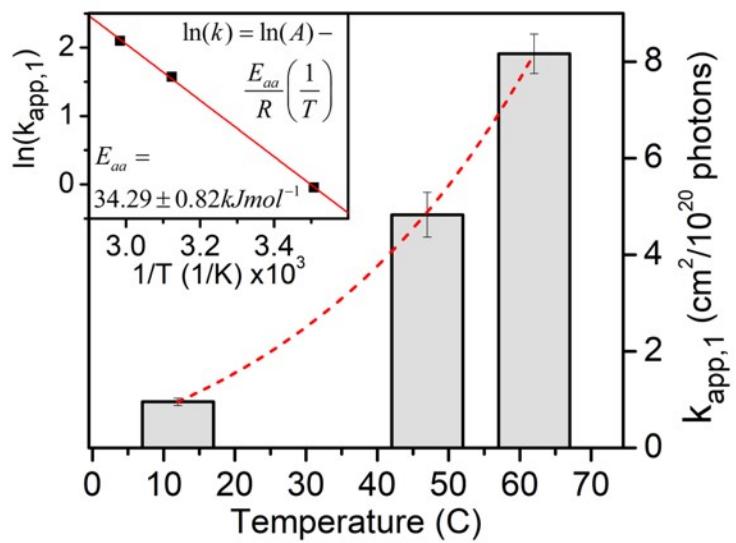


Figure S5. Apparent first-order rate constant as a function of reaction temperature for the photocatalytic reduction of selenate in SMIB with inset Arrhenius plot.

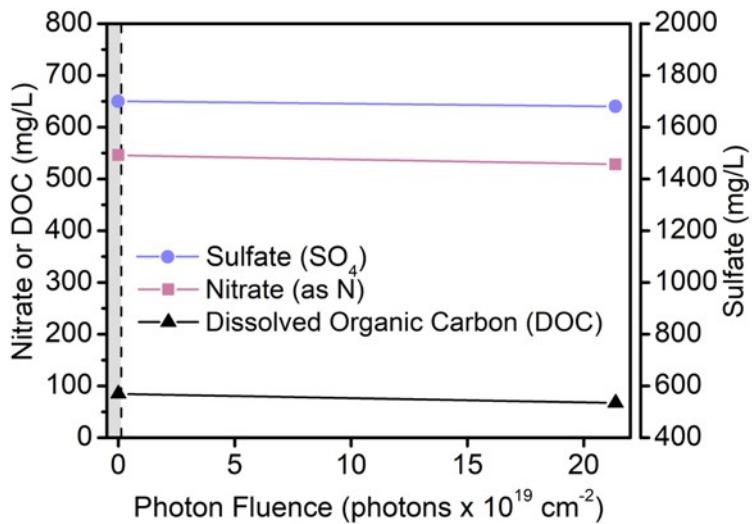


Figure S6. Nitrate, sulfate and dissolved organic carbon concentrations during the photocatalytic reduction of selenate in SMIB. Reaction conditions: 0.2 g L⁻¹ TiO₂, pH 4.5, 300 mg L⁻¹ formic acid and 37°C.

Response Surface Analysis

Table S2. Central composite design, experimental results, fitted values and residuals for the response surface study of the apparent first-order reaction rate constant with 4 center point replicates. Factor and level coding corresponds to **Table 1** in the main manuscript.

Run	Factor Levels					First Order Apparent Rate Constant, $k_{app,1}$ (cm ² /10 ²⁰ photons)	Fitted Values, $\hat{k}_{app,1}$ (cm ² /10 ²⁰ photons)	Residuals, e_i (cm ² /10 ²⁰ photons)	Standardized Residual, d_i
	x_1	x_2	x_1^2	x_2^2	x_1x_2				
1	-1	-1	1	1	1	0.991	0.746	0.245	0.120
2	1	-1	1	1	-1	5.179	4.844	0.336	0.164
3	-1	1	1	1	-1	1.575	1.341	0.234	0.114
4	1	1	1	1	1	7.004	6.680	0.324	0.159
5	-1.389	0	1.929	0	0	0.957	2.204	-1.247	-0.611
6	1.389	0	1.929	0	0	7.457	7.822	-0.365	-0.179
7	0	-1.413	0	1.996	0	1.173	1.461	-0.288	-0.141
8	0	1.413	0	1.996	0	2.906	3.179	-0.273	-0.134
9	0	0	0	0	0	4.890	4.641	0.250	0.122
10	0	0	0	0	0	7.422	4.641	2.782	1.363
11	0	0	0	0	0	3.356	4.641	-1.285	-0.630
12	0	0	0	0	0	2.895	4.641	-1.746	-0.855

Table S3. Analysis of variance for the response surface study of the apparent first-order reaction rate constant (Type III partial sum of squares). Factor coding corresponds to **Table 1** in the main manuscript.

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Squares	F-Value	p-Value
Regression	55.830	5	11.166	5.091	0.0362*
x_1	51.865	1	51.865	23.649	0.0028*
x_2	11.092	1	11.092	5.058	0.0655
x_1^2	7.208	1	7.208	3.287	0.1198
x_2^2	8.983	1	8.983	4.096	0.0894
x_1x_2	8.526	1	8.526	3.887	0.0961
Residual	13.159	6	2.193		
Lack of Fit	0.658	4	0.164	0.075	0.9872
Pure Error	12.501	2	6.251		
Total	69.488	11	6.317		

*Statistically significant ($p < 0.05$)

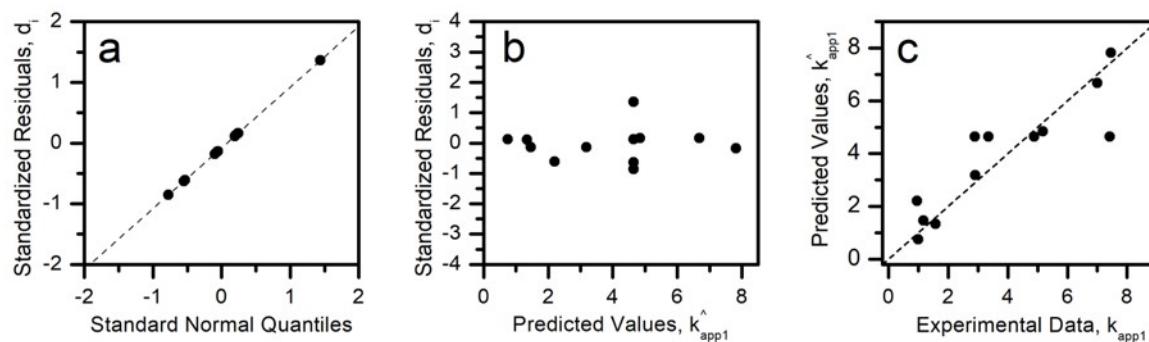


Figure S7. (a) Half-normal probability plot of residuals, (b) residual plot and (c) predicted vs actual apparent first-order rate constants for the response surface regression.

Table S4. Central composite design, experimental results, fitted values and residuals for the response surface study of the solid elemental Se selectivity with 4 center point replicates. Factor and level coding corresponds to **Table 1** in the main manuscript.

Run	Factor Levels					Selectivity to $\text{Se}^0_{(s)}$ @ 2.1×10^{20} photons cm^{-2} , $S(\text{Se}^0_{(s)})$ (no units)	Fitted Values, $\hat{S}(\text{Se}^0_{(s)})$ (no units)	Residuals, e_i (no units)	Standardized Residual, d_i
	x_1	x_2	x_1^2	x_2^2	x_1x_2				
1	-1	-1	1	1	1	0.832	0.883	-0.051	-0.438
2	1	-1	1	1	-1	0.069	0.050	0.019	0.163
3	-1	1	1	1	-1	0.966	0.894	0.071	0.611
4	1	1	1	1	1	0.913	0.771	0.142	1.212
5	-1.389	0	1.929	0	0	0.781	0.777	0.004	0.038
6	1.389	0	1.929	0	0	0.018	0.113	-0.095	-0.812
7	0	-1.413	0	1.996	0	0.641	0.600	0.041	0.354
8	0	1.413	0	1.996	0	0.985	1.117	-0.132	-1.129
9	0	0	0	0	0	0.436	0.574	-0.137	-1.174
10	0	0	0	0	0	0.610	0.574	0.037	0.314
11	0	0	0	0	0	0.713	0.574	0.139	1.189
12	0	0	0	0	0	0.535	0.574	-0.038	-0.329

Table S5. Analysis of variance for the response surface study of the solid elemental Se selectivity (Type III partial sum of squares). Factor coding corresponds to **Table 1** in the main manuscript.

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Squares	F-Value	p-Value
Regression	1.029	5	0.206	0.018	0.0038*
x_1	0.480	1	0.480	0.041	0.0016*
x_2	0.300	1	0.300	0.026	0.0051*
x_1^2	0.137	1	0.137	0.012	0.0272*
x_2^2	0.158	1	0.158	0.014	0.0204*
x_1x_2	0.158	1	0.158	0.014	0.0206*
Residual	0.097	6	0.016		
Lack of Fit	0.056	4	0.014	0.001	0.5337
Pure Error	0.041	2	0.020		
Total	1.125	11	0.102		

*Statistically significant ($p < 0.05$)

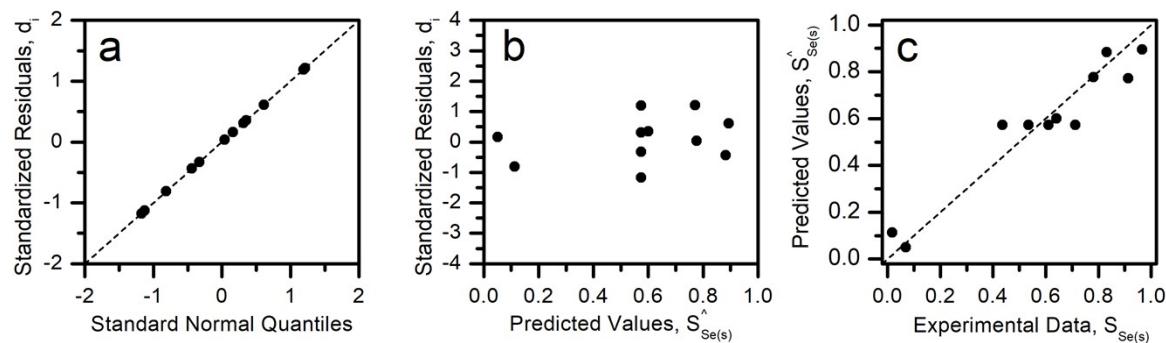


Figure S8. (a) Half-normal probability plot of residuals, (b) residual plot and (c) predicted vs actual solid elemental Se selectivity for the response surface regression.