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Supplementary material

Quantification of kinetic rate law parameters of uranium release from sodium autunite as a function of aqueous bicarbonate concentrations

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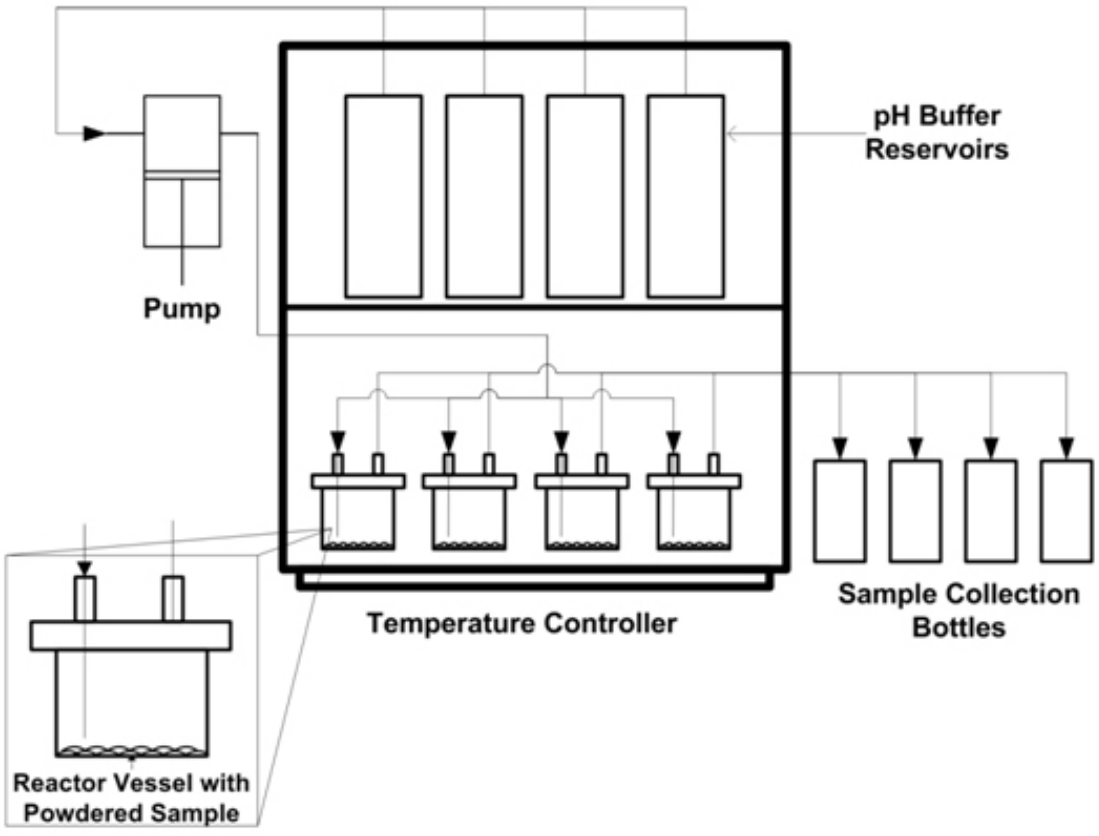

Fig. S1. Schematic of single-pass flow-through experimental setup showing syringe pump, reactor vessels, temperature chamber, buffer reservoirs and sample collection bottles.

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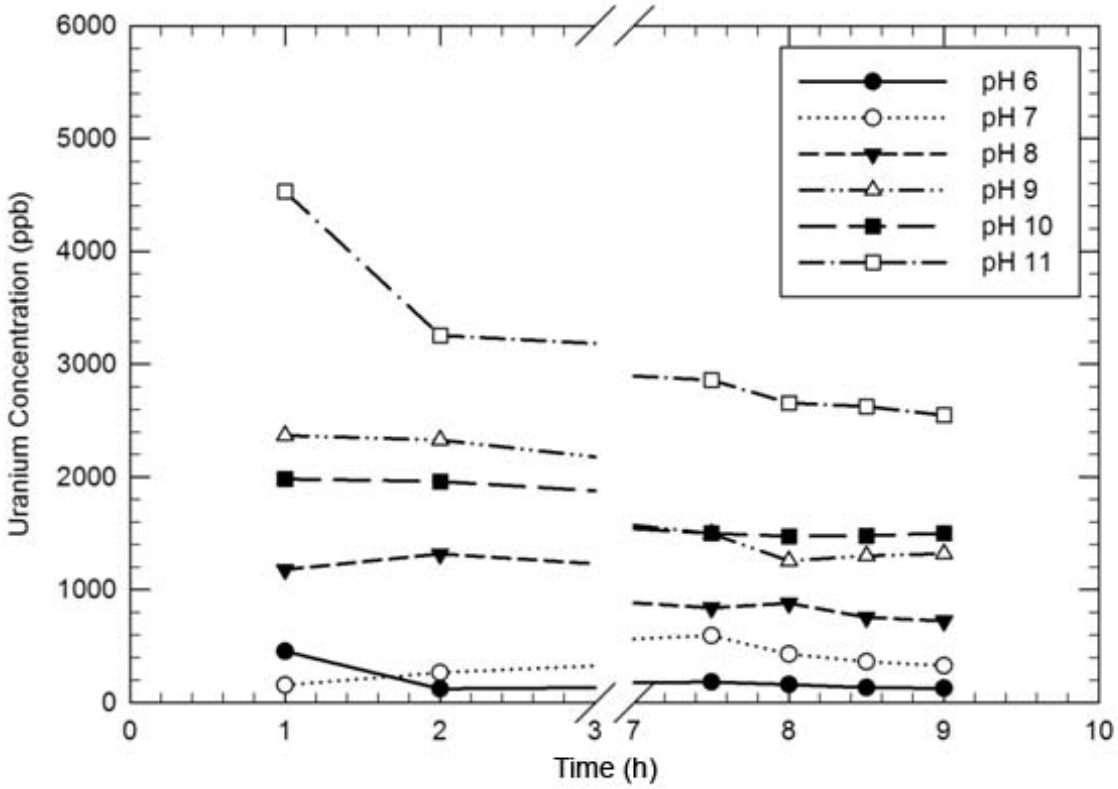

Fig. S2. Change in uranium concentration over time for SPTF experiments for Na-autunite at 23 °C, 0.0005 M HCO_3^- and pH range 6–11

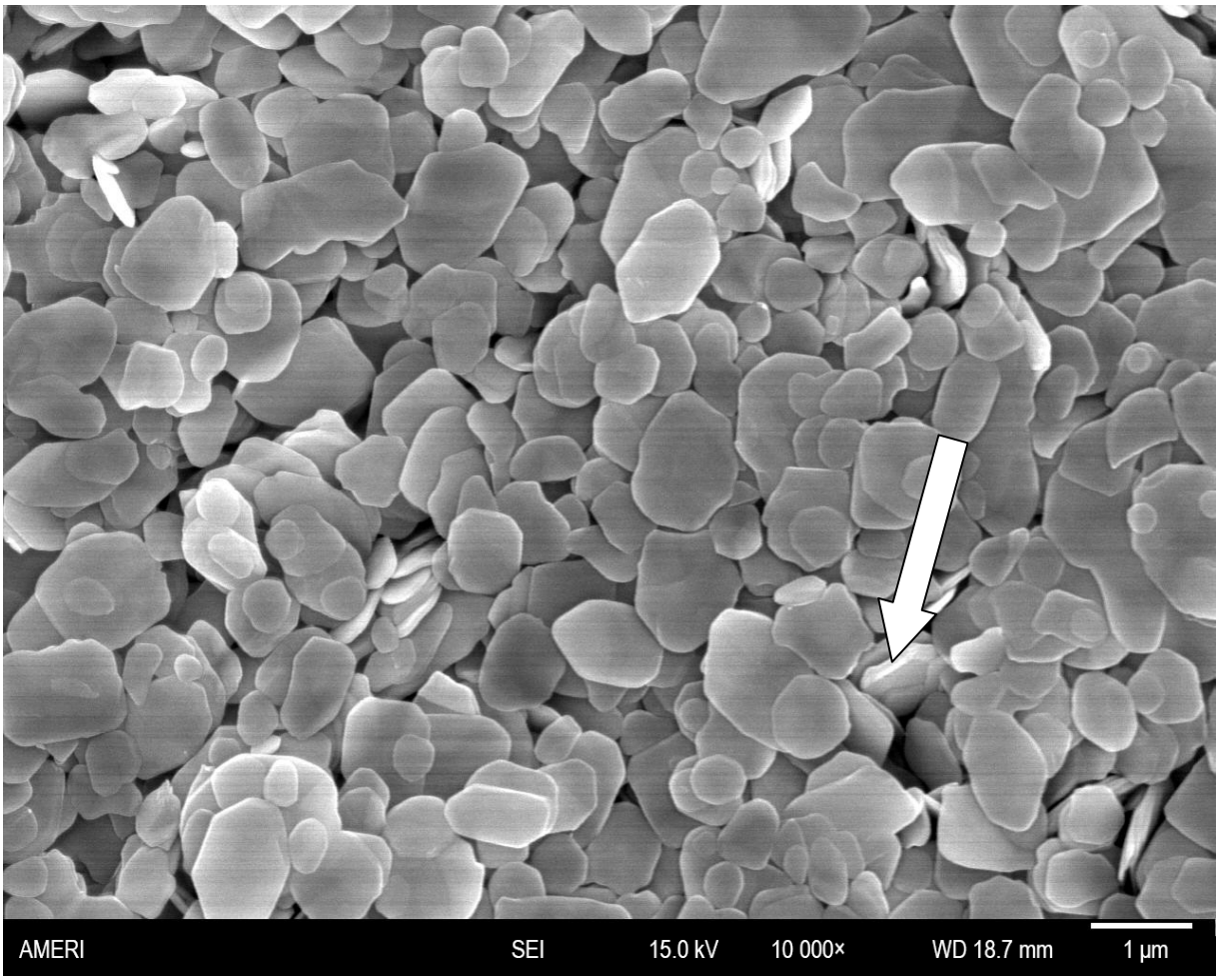

Fig. S3. Image of post-reacted Na-autunite minerals at 10 000 magnification showing no formation of secondary mineral phases and minor formation of cleavage planes (black arrow) occurred during the dissolution process.

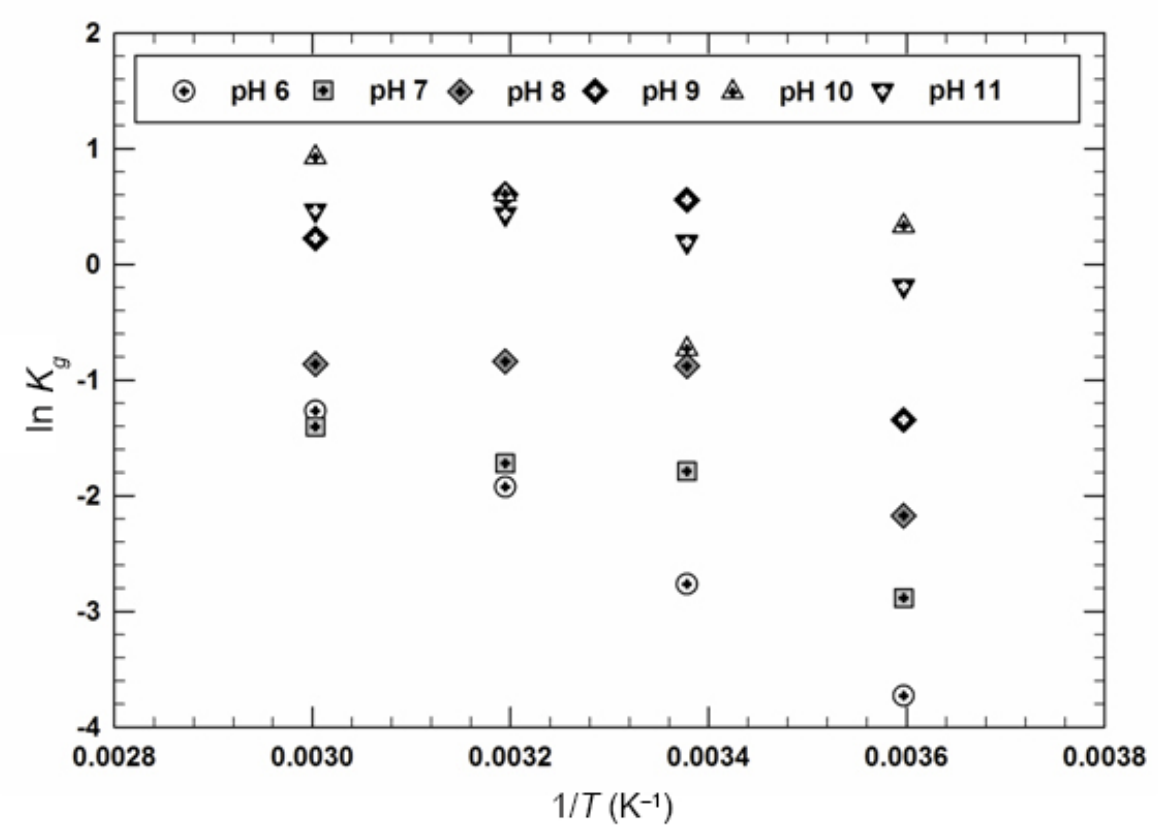

Fig. S4. Normal logarithm of pseudo equilibrium constant as a function of inverse temperature. The resulting regression lines yield the values of enthalpy (ΔH)

Table S1. Composition of Tris-buffered bicarbonate solutions used in synthetic Na-autunite dissolution studies

Solution	Composition	pH @ 23°C
1	0.01 M Tris + 0.0005 M HCO_3^- + 0.01096 M HCl	5.96
2	0.01 M Tris + 0.0005 M HCO_3^- + 0.0103M HCl	7.00
3	0.01 M Tris + 0.0005 M HCO_3^- + 0.00779 M HCl	8.01
4	0.01 M Tris + 0.0005 M HCO_3^- + 0.00256 M HCl	9.01
5	0.01 M Tris + 0.0005 M HCO_3^- + 0.000147 M HCl	10.02
6	0.01 M Tris + 0.0005 M HCO_3^- + 0.00083 M KOH	11.00
7	0.01 M Tris + 0.001 M HCO_3^- + 0.0112 M HCl	6.01
8	0.01 M Tris + 0.001 M HCO_3^- + 0.0103 M HCl	7.02
9	0.01 M Tris + 0.001 M HCO_3^- + 0.00654 M HCl	8.00
10	0.01 M Tris + 0.001 M HCO_3^- + 0.00265 M HCl	9.01
11	0.01 M Tris + 0.001 M HCO_3^- + 0.000147 M HCl	10.00
12	0.01 M Tris + 0.001 M HCO_3^- + 0.00116 M KOH	11.00
13	0.01 M Tris + 0.002 M HCO_3^- + 0.0118 M HCl	6.01
14	0.01 M Tris + 0.002 M HCO_3^- + 0.0108 M HCl	6.99
15	0.01 M Tris + 0.002 M HCO_3^- + 0.00798 M HCl	7.99
16	0.01 M Tris + 0.002 M HCO_3^- + 0.00267 M HCl	9.01
17	0.01 M Tris + 0.002 M HCO_3^- + 0.00006 M KOH	10.00
18	0.01 M Tris + 0.002 M HCO_3^- + 0.00192 M KOH	11.00
19	0.01 M Tris + 0.003 M HCO_3^- + 0.0125 M HCl	6.01
20	0.01 M Tris + 0.003 M HCO_3^- + 0.01077 M HCl	7.01
21	0.01 M Tris + 0.003 M HCO_3^- + 0.00784 M HCl	8.01
22	0.01 M Tris + 0.003 M HCO_3^- + 0.00240 M HCl	9.01
23	0.01 M Tris + 0.003 M HCO_3^- + 0.000379 M KOH	9.99
24	0.01 M Tris + 0.003 M HCO_3^- + 0.002747 M KOH	11.00

Table S2. Aqueous speciation reactions used in modelling

Speciation reaction	log K	Source
$UO_2^{2+} + 3CO_3^{-2} = UO_2(CO_3)_2^{-2}$	16.61	[1]
$UO_2^{2+} + 3CO_3^{-2} = UO_2(CO_3)_3^{-4}$	21.84	[1]
$UO_2^{2+} + H_2O = UO_2(OH)^+ + H^+$	–5.25	[1]
$UO_2^{2+} + 2H_2O = UO_2(OH)_2(aq) + 2H^+$	–12.15	[1]
$UO_2^{2+} + 3H_2O = UO_2(OH)_3^- + 3H^+$	–20.25	[1]
$UO_2^{2+} + 4H_2O = UO_2(OH)_4^{-2} + 4H^+$	–32.4	[1]
$2UO_2^{2+} + H_2O = (UO_2)_2(OH)^{3+} + H^+$	–2.7	[1]
$2UO_2^{2+} + 2H_2O = (UO_2)_2(OH)_2^{2+} + 2H^+$	–5.62	[1]
$3UO_2^{2+} + 4H_2O = (UO_2)_3(OH)_4^{2+} + 4H^+$	–11.9	[1]
$3UO_2^{2+} + 5H_2O = (UO_2)_3(OH)_5^+ + 5H^+$	–15.55	[1]
$3UO_2^{2+} + 6CO_3^{-2} = (UO_2)_3(CO_3)_6^{-6}$	54.0	[1]
$3UO_2^{2+} + 7H_2O = (UO_2)_3(OH)_7^- + 7H^+$	–32.2	[1]
$4UO_2^{2+} + 7H_2O = (UO_2)_4(OH)_7^+ + 7H^+$	–21.9	[1]
$H_2CO_3 = H^+ + HCO_3^-$	–6.35	[1]
$H_2CO_3 = 2H^+ + CO_3^{-2}$	–16.68	[1]
$H^+ + PO_4^{-3} = HPO_4^{-2}$	12.375	[2]
$K^+ + H^+ + PO_4^{-3} = KHPO_4^-$	13.25	[2]
$2K^+ + H^+ + PO_4^{-3} = K_2HPO_4(aq)$	13.5	[2]
$UO_2^{2+} + PO_4^{-3} = UO_2PO_4^-$	13.23	[2]
$UO_2^{2+} + PO_4^{-3} + H^+ = UO_2HPO_4(aq)$	19.61	[2]
$UO_2^{2+} + PO_4^{-3} + 2H^+ = UO_2H_2PO_4^+$	20.69	[2]
$UO_2^{2+} + PO_4^{-3} + 3H^+ = UO_2H_3PO_4^{2+}$	22.48	[2]

Table S3. Single-Pass flow-through experimental conditions and dissolution rates of synthetic sodium autunite

Sample ID	Surface area (m^2)	Temperature (°C)	pH (23 °C)	Flow rate (mL day^{-1})	U (μg L^{-1})	U rate (mol m^{-2} s^{-1})	
			0.0005 M HCO_3^-				
SAUT-01	1.07	5	6	1014	24.3	2.74×10^{-12}	(5.31×10^{-13})
SAUT-02	1.09	5	7	1021	41.2	3.600×10^{-12}	(6.98×10^{-13})
SAUT-03	1.03	5	8	1022	79.5	7.02×10^{-12}	(1.36×10^{-12})
SAUT-04	0.97	5	9	976	404.8	3.66×10^{-11}	(7.10×10^{-12})
SAUT-05	0.65	5	10	1020	2057.8	2.94×10^{-10}	(4.09×10^{-11})
SAUT-06	0.59	5	11	1003	414.7	6.30×10^{-11}	(1.22×10^{-11})
SAUT-07	1.59	23	6	1016	245.9	1.9×10^{-12}	(3.69×10^{-13})
SAUT-08	1.18	23	7	976	279.4	2.084×10^{-11}	(4.036×10^{-12})
SAUT-09	1.59	23	8	952	1025.2	2.54×10^{-11}	(1.45×10^{-11})
SAUT-10	1.18	23	9	1030	1075.8	8.55×10^{-11}	(2.46×10^{-11})
SAUT-11	1.60	23	10	822	2070.4	7.83×10^{-11}	(8.77×10^{-12})
SAUT-12	1.59	23	11	997	2799.0	1.12×10^{-10}	(2.17×10^{-11})
SAUT-13	0.89	40	6	1483	85.6	1.28×10^{-11}	(2.49×10^{-12})
SAUT-14	0.89	40	7	1500	177.7	2.685×10^{-11}	(5.19×10^{-12})
SAUT-15	1.63	40	8	1474	496.0	4.06×10^{-11}	(1.43×10^{-11})
SAUT-16	0.88	40	9	1513	706.7	1.10×10^{-10}	(2.12×10^{-11})
SAUT-17	1.58	40	10	1512	1652.9	1.43×10^{-10}	(3.84×10^{-11})
SAUT-18	1.12	40	11	1508	1161.0	1.33×10^{-10}	(2.58×10^{-11})
SAUT-19	0.88	60	6	1910	68.6	1.32×10^{-11}	(2.55×10^{-12})
SAUT-20	1.61	60	7	2429	214.9	2.94×10^{-11}	(7.92×10^{-12})
SAUT-21	1.14	60	8	2448	640.7	1.24×10^{-11}	(2.41×10^{-12})
SAUT-22	0.89	60	9	2425	1766.7	4.35×10^{-11}	(6.46×10^{-11})
SAUT-23	1.16	60	10	2442	1816.2	3.52×10^{-10}	(6.81×10^{-11})
SAUT-24	0.89	60	11	2435	681.9	1.90×10^{-10}	(3.68×10^{-11})
			0.001 M HCO_3^-				
SAUT-25	0.46	5	6	990	9.573	1.94×10^{-12}	(1.98×10^{-13})
SAUT-26	0.77	5	7	989	32.123	3.70×10^{-12}	(7.16×10^{-13})
SAUT-27	0.77	5	8	1003	99.458	1.18×10^{-11}	(2.28×10^{-12})
SAUT-28	0.76	5	9	1021	414.558	5.04×10^{-11}	(9.76×10^{-12})
SAUT-29	0.69	5	10	1002	2131.330	2.79×10^{-10}	(3.88×10^{-11})
SAUT-30	0.55	5	11	986	683.31	1.10×10^{-10}	(2.12×10^{-11})
SAUT-31	1.17	23	6	976	14.4	1.4×10^{-12}	(2.1×10^{-13})
SAUT-32	0.88	23	7	973	48.5	2.47×10^{-11}	(6.99×10^{-13})

Sample ID	Surface area (m^2)	Temperature (°C)	pH (23 °C)	Flow rate ($mL\ day^{-1}$)	U ($\mu g\ L^{-1}$)	U rate ($mol\ m^{-2}\ s^{-1}$)	
SAUT-33	1.18	23	8	980	654.0	3.58×10^{-11}	(5.98×10^{-12})
SAUT-34	1.18	23	9	971	1605.6	1.27×10^{-10}	(2.46×10^{-11})
SAUT-35	0.88	23	10	1001	799.9	8.23×10^{-11}	(8.77×10^{-12})
SAUT-36	1.14	23	11	1000	1303.3	1.00×10^{-10}	(1.94×10^{-11})
SAUT-37	0.88	40	6	1509	102.6	1.59×10^{-11}	(3.09×10^{-12})
SAUT-38	0.88	40	7	1514	191.4	2.99×10^{-11}	(5.80×10^{-12})
SAUT-39	0.88	40	8	1518	315.4	5.36×10^{-11}	(9.54×10^{-12})
SAUT-40	0.89	40	9	1528	832.0	1.09×10^{-10}	(2.12×10^{-11})
SAUT-41	1.59	40	10	1495	1589.8	1.88×10^{-10}	(2.61×10^{-11})
SAUT-42	1.13	40	11	1507	1548.1	1.92×10^{-10}	(3.71×10^{-11})
SAUT-43	0.89	60	6	2430	21.2	7.15×10^{-12}	(1.35×10^{-12})
SAUT-44	0.87	60	7	2443	64.9	3.64×10^{-11}	(2.44×10^{-12})
SAUT-45	1.12	60	8	2412	194.3	3.78×10^{-11}	(7.33×10^{-12})
SAUT-46	1.16	60	9	2452	615.2	1.17×10^{-10}	(2.26×10^{-11})
SAUT-47	1.13	60	10	2442	2433.2	4.60×10^{-10}	(9.21×10^{-11})
SAUT-48	1.55	60	11	2447	1757.6	2.50×10^{-10}	(4.85×10^{-11})
				0.002 M HCO_3^-			
SAUT-49	0.61	5	6	977	20.3	2.95×10^{-12}	(4.11×10^{-13})
SAUT-50	0.84	5	7	1037	68.2	7.65×10^{-12}	(1.48×10^{-12})
SAUT-51	1.03	5	8	1019	152.6	1.37×10^{-11}	(2.65×10^{-12})
SAUT-52	0.82	5	9	976	551.1	5.90×10^{-11}	(1.14×10^{-11})
SAUT-53	0.59	5	10	1003	2060	3.13×10^{-10}	(4.36×10^{-11})
SAUT-54	0.59	5	11	1004	946.1	1.49×10^{-10}	(2.89×10^{-11})
SAUT-55	0.88	23	6	994	13.9	1.73×10^{-12}	(2.08×10^{-13})
SAUT-56	1.18	23	7	961	388.2	2.86×10^{-11}	(5.54×10^{-12})
SAUT-57	1.18	23	8	966	393.1	3.59×10^{-11}	(6.34×10^{-12})
SAUT-58	1.59	23	9	955	3851.3	2.12×10^{-10}	(5.57×10^{-11})
SAUT-59	1.12	23	10	976	1727.2	1.35×10^{-10}	(1.88×10^{-11})
SAUT-60	0.89	23	11	978	1154.2	1.16×10^{-10}	(2.21×10^{-11})
SAUT-61	0.88	40	6	1492	191.4	2.70×10^{-11}	(5.23×10^{-12})
SAUT-62	0.86	40	7	1504	265.5	4.17×10^{-11}	(8.09×10^{-12})
SAUT-63	0.86	40	8	1506	460.3	7.26×10^{-11}	(1.40×10^{-11})
SAUT-64	0.87	40	9	1517	1576.9	2.49×10^{-10}	(4.83×10^{-11})
SAUT-65	1.63	40	10	1512	3386.3	2.77×10^{-10}	(5.40×10^{-11})
SAUT-66	1.14	40	11	1502	2196.0	2.62×10^{-10}	(5.07×10^{-11})

Sample ID	Surface area (m^2)	Temperature (°C)	pH (23 °C)	Flow rate (mL day^{-1})	U (μg L^{-1})	U rate (mol m^{-2} s^{-1})	
SAUT-67	0.86	60	6	2432	55.7	1.86×10^{-11}	(2.11×10^{-12})
SAUT-68	1.15	60	7	2450	241.3	4.65×10^{-11}	(9.01×10^{-12})
SAUT-69	1.14	60	8	2455	203.4	4.64×10^{-11}	(7.65×10^{-12})
SAUT-70	0.89	60	9	2440	633.5	1.75×10^{-10}	(2.33×10^{-11})
SAUT-71	0.88	60	10	2445	1833.1	4.70×10^{-10}	(6.78×10^{-11})
SAUT-72	1.17	60	11	2430	1723.1	3.23×10^{-10}	(6.26×10^{-11})
				0.003 M HCO_3^-			
SAUT-73	0.60	5	6	1016	34.7	5.41×10^{-12}	(7.52×10^{-13})
SAUT-74	0.83	5	7	990	92.8	9.85×10^{-12}	(1.91×10^{-12})
SAUT-75	0.82	5	8	994	204.2	2.22×10^{-11}	(4.31×10^{-12})
SAUT-76	0.88	5	9	973	709.5	7.08×10^{-11}	(1.37×10^{-11})
SAUT-77	0.64	5	10	973	3380.0	4.64×10^{-10}	(6.45×10^{-11})
SAUT-78	0.65	5	11	995	1218.6	1.69×10^{-10}	(3.28×10^{-11})
SAUT-79	1.19	23	6	986	150.8	9.88×10^{-12}	(2.18×10^{-12})
SAUT-80	1.19	23	7	995	427.9	4.23×10^{-11}	(6.25×10^{-12})
SAUT-81	0.88	23	8	1001	798.8	8.13×10^{-11}	(1.21×10^{-11})
SAUT-82	0.89	23	9	982	1329.5	1.55×10^{-10}	(2.57×10^{-11})
SAUT-83	1.12	23	10	982	1487.4	1.17×1010	(1.63×10^{-11})
SAUT-84	0.89	23	11	978	2670.8	2.64×10^{-10}	(3.92×10^{-11})
SAUT-85	0.87	40	6	1501	188.1	2.94×10^{-11}	(5.69×10^{-12})
SAUT-86	0.87	40	7	1508	305.1	4.76×10^{-11}	(9.22×10^{-12})
SAUT-87	1.14	40	8	1501	1113.4	1.32×10^{-10}	(2.56×10^{-11})
SAUT-88	1.12	40	9	1504	2748.5	3.31×10^{-10}	(6.42×10^{-11})
SAUT-89	0.87	40	10	1477	1665.9	2.54×10^{-10}	(3.77×10^{-11})
SAUT-90	1.15	40	11	1512	2737.6	3.26×10^{-10}	(6.31×10^{-11})
SAUT-91	1.15	60	6	2431	238.9	4.58×10^{-11}	(8.86×10^{-12})
SAUT-92	1.59	60	7	2442	310.8	6.00×10^{-11}	(1.16×10^{-11})
SAUT-93	0.86	60	8	2432	274.9	6.98×10^{-11}	(1.03×10^{-11})
SAUT-94	0.87	60	9	2426	743.7	2.04×10^{-10}	(2.76×10^{-11})
SAUT-95	0.86	60	10	2429	2736.3	6.98×10^{-10}	(1.03×10^{-10})
SAUT-96	1.14	60	11	2421	2026.7	3.89×10^{-10}	(7.53×10^{-11})

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