ZINC ADSORPTION EFFECTS ON ARSENITE OXIDATION KINETICS AT THE BIRNESSITE-WATER INTERFACE

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		% As as [.	As(III)](a	$(\mathbf{q})^{1}$	
	$\left[As(III)\right]_{i} = 1$	00 μΜ		300 µM	
No Zn	Pre-sorbed	Simultaneous	No Zn	Pre-sorbed	Simultaneous
100.0	100.0	100.0	100.0	100.0	100.0
68.5	93.9	91.6	84.3	96.6	92.7
44.1	89.0	83.4	68.4	90.1	87.1
28.0	83.1	74.0	56.2	81.6	76.8
2.7	64.5	44.9	36.3	62.9	54.8
0.0	32.0	5.9	20.0	39.9	30.9
0.0	18.0	0.0	14.6	28.0	19.7
0.0	9.6	0.0	8.1	25.2	18.5
0.0	2.0	0.0	NA	19.0	NA
0.4	5.0	0.0	0.4	11.3	0.8
	No Zn 100.0 68.5 44.1 28.0 2.7 0.0 0.0 0.0 0.0 0.0 0.0 0.0	$\begin{bmatrix} As(III) \end{bmatrix}_{i} = 1 \\ \hline No Zn & Pre-sorbed \\ \hline 100.0 & 100.0 \\ \hline 68.5 & 93.9 \\ \hline 44.1 & 89.0 \\ \hline 28.0 & 83.1 \\ \hline 2.7 & 64.5 \\ \hline 0.0 & 32.0 \\ \hline 0.0 & 18.0 \\ \hline 0.0 & 9.6 \\ \hline 0.0 & 2.0 \\ \hline 0.4 & 5.0 \\ \end{bmatrix}$	% As as [[As(III)]_i = 100 μ MNo ZnPre-sorbedSimultaneous100.0100.0100.068.593.991.644.189.083.428.083.174.02.764.544.90.032.05.90.018.00.00.09.60.00.02.00.00.45.00.0	% As as [As(III)](a[As(III)]_i = 100 μ M[As(III)]_i = 100 μ MNo ZnNo ZnPre-sorbedSimultaneousNo Zn100.0100.0100.0100.068.593.991.684.344.189.083.468.428.083.174.056.22.764.544.936.30.032.05.920.00.018.00.014.60.09.60.08.10.02.00.0NA0.45.00.00.4	% As as $[As(III)](aq)^1$ $[As(III)]_i = 100 \ \mu M$ $[As(III)]_i =$ No ZnPre-sorbedSimultaneousNo ZnPre-sorbed100.0100.0100.0100.0100.0100.068.593.991.684.396.644.189.083.468.490.128.083.174.056.281.62.764.544.936.362.90.032.05.920.039.90.018.00.014.628.00.02.00.0NA19.00.45.00.00.411.3

Table 1. Percent As(III)(aq) during As(III) oxidation at the birnessite-water interface as a function of initial As(III) concentrations, various Zn(II) additions (i.e., no Zn(II), Zn(II) pre-sorbed prior to the As(III) addition, and As(III)/Zn(II) simultaneous addition) at pH 4.5.

 $^{1}NA = Not Available$

		% As as [4	As(III)](a	q) ¹	
	$\left[As(III)\right]_{i} = 1$	00 μΜ		300 µM	
No Zn	Pre-sorbed	Simultaneous	No Zn	Pre-sorbed	Simultaneous
100.0	100.0	100.0	100.0	100.0	100.0
79.8	98.6	92.5	90.3	98.0	97.1
68.5	96.3	92.2	82.9	97.7	95.6
55.3	93.3	88.8	80.9	97.7	94.2
42.6	90.8	85.2	73.6	94.4	91.4
19.5	80.5	75.7	62.9	88.7	87.8
16.3	77.8	71.3	55.5	83.7	79.7
NA	70.0	62.3	46.7	77.8	74.2
NA	65.9	52.8	NA	71.9	68.9
3.5	19.6	18.8	25.7	46.8	45.3
	No Zn 100.0 79.8 68.5 55.3 42.6 19.5 16.3 NA NA 3.5	[As(III)] _i = 1 No Zn Pre-sorbed 100.0 100.0 79.8 98.6 68.5 96.3 55.3 93.3 42.6 90.8 19.5 80.5 16.3 77.8 NA 70.0 NA 65.9 3.5 19.6	% As as [[As(III)]_i = 100 μ MNo ZnPre-sorbedSimultaneous100.0100.0100.079.898.692.568.596.392.255.393.388.842.690.885.219.580.575.716.377.871.3NA70.062.3NA65.952.83.519.618.8	% As as [As(III)](a[As(III)]_i = 100 μ M[As(III)]_i = 100 μ MNo ZnPre-sorbedSimultaneousNo Zn100.0100.0100.0100.079.898.692.590.368.596.392.282.955.393.388.880.942.690.885.273.619.580.575.762.916.377.871.355.5NA70.062.346.7NA65.952.8NA3.519.618.825.7	% As as $[As(III)](aq)^{1}$ $[As(III)]_{i} = 100 \ \mu M$ $[As(III)]_{i} =$ No ZnPre-sorbedSimultaneousNo ZnPre-sorbed100.0100.0100.0100.0100.0100.079.898.692.590.398.068.596.392.282.997.755.393.388.880.997.742.690.885.273.694.419.580.575.762.988.716.377.871.355.583.7NA70.062.346.777.8NA65.952.8NA71.93.519.618.825.746.8

Table 2. Percent As(III)(aq) during the As(III) oxidation at the birnessite-water interface as a function of initial As(III) concentrations and various Zn(II) additions (i.e., no Zn(II), Zn(II) pre-sorbed prior to the As(III) addition, and As(III)/Zn(II) simultaneous addition) at pH 6.

 $^{1}NA = Not Available$

Table 3. Log of Ion Activity Product (IAP) and Log of Solubility Product (Log K) for Mn(II)- and Zn(II)-arsenate precipitates during
the As(III) oxidation kinetic experiments on birnessite.Time (h)

							1					
	Mn ₃ (<i>i</i>	$AsO_4)_2$	Mn ₃ (AsC	04)2·8H2O	Zn ₃ (A:	$sO_4)_2^a$	$Zn_3(AsO_4$	$_{1})_{2}\cdot 5H_{2}O^{a}$	Zn ₃ (As	$O_4)_2^b$	Zn ₃ (AsO ₄	$)_2 \cdot 5H_2O^b$
	pH4.5	pH6	pH4.5	pH6	pH4.5	pH6	pH4.5	pH6	pH4.5	pH6	pH4.5	pH6
					[As(]	$[II]_i = I$	<i>Μ</i> π 00,					
0.67	13.4	NA	13.1	48.0	14.3	14.7	15.4	12.9	13.6	12.7	14.7	10.9
7	11.9	12.5	11.6	9.3	12.9	13.2	13.9	11.3	12.4	12.5	13.4	10.6
4	11.7	11.0	11.4	7.8	12.1	12.2	13.2	10.4	11.8	11.8	12.9	10.0
8	11.8	10.3	11.5	7.1	11.8	11.1	12.9	9.3	11.7	11.0	12.7	9.2
12	11.8	9.9	11.5	6.7	11.8	10.5	12.8	8.6	11.7	10.5	12.7	8.7
24	11.8	9.7	11.5	6.5	11.7	9.5	12.8	T.T	11.7	9.8	12.7	8.0
					[As($[II]_i = 3$	00 JuM					
0.67	11.8	17.6	11.4	14.4	13.2	13.9	14.2	12.1	12.7	12.6	13.8	10.8
0	9.6	10.4	9.6	5.2	11.6	12.6	12.7	10.7	11.3	12.0	12.4	10.2
4	9.2	8.9	8.9	4.4	11.1	11.5	12.1	9.6	10.9	11.1	11.9	9.3
8	8.9	7.8	8.6	3.7	10.9	10.3	11.9	8.5	10.7	10.2	11.7	8.4
12	8.8	7.4	8.4	3.5	10.7	9.8	11.8	8.0	10.6	9.7	11.6	7.9
24	8.6	6.9	8.2	3.0	10.7	8.9	11.7	7.1	10.5	9.0	11.5	7.2
For comp:	trison -log	$g(K_{sadiq})$ 1	for Mn ₃ (A	$(O_4)_2 = -8.2$	5, -log(K	mineq1+) fo	or Mn ₃ (AsC	$(4)_2 \cdot 8H_2O =$: -28.9, -10	og(Ksadiq) for Zn ₃ (A	$SO_4)_2 = -$
8.2, and -l	og(K mineq	(1+) for Zr	n ₃ (AsO ₄) ₂ ·:	$5H_2O = -27$	7.6. ^a Pre-	sorbed 2	Zn(II) for 24	th prior to	the As(II	I) additid	on.	

4 ^bZn(II) and As(III) simultaneous addition.



Figure 1. Effects of pre-sorbed Zn(II) vs Zn(II)/As(III)-simultaneous treatment on the As(III) oxidation kinetics on birnessite surfaces (pH 6, suspension density = 0.1 g L⁻¹, I = 0.01 M NaCl, total Zn(II) concentrations: $[Zn]_t = 100 \,\mu\text{M}$, and N₂ atmosphere). Percent As(III) depletion, As(V) release, and total As adsorption are shown as a function of time (h). (a) initial As(III) concentrations: $[As(III)]_i = 100 \,\mu\text{M}$; (b) $[As(III)]_i = 300 \,\mu\text{M}$.



Figure 2. Effects of the pre-sorbed Zn(II) vs Zn(II)/As(III)-simultaneous treatment on the aqueous profiles of Zn(II) during the As(III) oxidation kinetics on birnessite surfaces (pH 6, suspension density = 0.1 g L⁻¹, I = 0.01 M NaCl, total Zn(II) concentrations: [Zn]_t = 100 μ M, and N₂ atmosphere). (a) Initial As(III) concentrations: [As(III)]_i = 100 μ M; (b) [As(III)]_i = 300 μ M.