# **APPENDIX I**

## PH AMENDMENT EVALUATION

- 1.1 CAP pH MODEL MEMO
- 1.2 SIDERITE LEACHATE EVALUATION

## **I.1**

# **CAP pH MODEL MEMO**

# **APPENDIX I**

## PH AMENDMENT EVALUATION

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## **I.1**

# **CAP pH MODEL MEMO**



# MEMORANDUM

То:	Caryn Kiehl-Simpson (Parsons)	Date:	April 3, 2012				
From:	Minna Swanson-Theisen and Dimitri	Project:	Onondaga Lake Cap/				
	Vlassopoulos		Dredge Final Design				
Cc:	Ed Glaza (Parsons), Paul La Rosa						
Re:	Siderite Dose Estimates for pH-Amended Sediment Cap Areas						

This memorandum presents the recommended dose of siderite amendment for porewater pH control in areas of Onondaga Lake where sediments are impacted by hyperalkaline wastes and capping will be implemented as part of the final remedy. Siderite dose estimates were developed for parts of Remediation Areas A, B, C, D (ILWD), Waste Beds 1-8, and Waste Bed B. The area-specific siderite dose estimates account for spatial variability of porewater pH, upwelling velocities, and porewater expression during initial consolidation of capped sediments.

This report is organized into six sections. Section 1 provides background information on the design of the cap for control of pH and objectives of the present work. Section 2 gives a description of the cap pH model and modifications implemented for the current effort. Section 3 describes the model scenarios investigated. Section 4 presents the simulation results for the different cap areas. Section 5 discusses the sensitivity of cap pH amendment effectiveness to vertical distribution of siderite. Finally, Section 6 presents the recommended minimum siderite ore dose rates for the various cap areas.

#### 1 Background

Figure 1 illustrates the conceptual model of the sediment cap adopted for the final design cap pH modeling. The cap is emplaced directly on top of contaminated sediments and has a total thickness of 2 feet 3 inches (68 cm) as modeled. It is divided into three layers, from bottom to top: (1) a 6-inch (15 cm) thick pH amendment layer where the bottom 3-inches is dedicated to the mixing layer and the top 3-inches is dedicated to chemical isolation, (2) an additional 9-inch (23 cm) thick chemical isolation layer which is amended with granular activated carbon (GAC), and (3) a 12-inch (30 cm) thick habitat layer.

Previous modeling conducted as part of the Cap Intermediate Design developed a preliminary estimate for siderite dose in the cap areas containing in-lake waste deposits (ILWD) (Parsons, 2011). Refinements to the model for purposes of the final design include area specific estimates of siderite application based on pH and groundwater upwelling velocities (Appendix B and Appendix C) specific to each area as well as estimates of initial consolidation (Appendix H) following cap placement. The design criteria, developed in consultation with DEC, are as follows:

- 1) Porewater pH will be neutralized to values less than 8 within the upper part of the cap including the upper half of the siderite-amended layer (i.e. the upper three inches of the six inch thick amendment layer) within a few years after cap construction; and
- 2) Porewater pH shall remain below 8 within the chemical isolation and habitat layers for 1,000 years.

## 2 Cap pH Model

The geochemical reactive transport model used to simulate porewater pH evolution in the siderite-amended sediment cap is described in detail in Appendix I of the Intermediate Design Report (Parsons, 2011) and is briefly summarized here. The model is constructed using PHREEQC (Parkhurst & Appelo 1999) with the *llnl.dat* thermodynamic database. Modifications were made to the model domain to reflect changes between the intermediate and final cap designs, as described below.

The sediment cap model domain consists of three layers as shown in Figure 1: (1) a 6-inch thick pH amendment layer (siderite-amended sand), (2) a 9-inch thick GAC-amended sand layer (for contaminant sorption), and (3) a 12-inch thick habitat layer (sand). The porosity of the cap is assumed to be 0.40 based on bench scale porosity testing results, as discussed in Appendix B. The mass of siderite added to the pH amendment layer can be varied in order to simulate the effect of siderite dose on cap pH performance.

The cap-water interface is the upper boundary condition in the model and is represented by a fixed concentration boundary with chemical characteristics of Onondaga Lake water. The lower boundary condition is a time-varying flow and concentration boundary representing hyperalkaline porewater. The chemical compositions of lake water and porewater used in the model are given in Table 1. Time-dependent advective flux of hyperalkaline porewater is modeled to account for both groundwater upwelling and porewater expression due to sediment consolidation after cap emplacement. Initially, the porewater flux is dominated by consolidation, and transitions over time to the steady-state upwelling flux.

The model accounts for the dissolution of siderite (FeCO<sub>3</sub>), and precipitation of the main reaction products, hydrous iron oxide (FeOOH) and calcite (CaCO<sub>3</sub>). The dissolved iron produced by siderite dissolution reacts with hydroxyl (OH<sup>-</sup>) ions in porewater, precipitating hydrous iron oxide and lowering pH. The dissolved carbonate ions produced from siderite dissolution react with calcium in the porewater, leading to precipitation of calcite which buffers the pH at circum-neutral values.

The model includes options for modeling the carbonate mineral reactions as either kinetic or chemical equilibrium processes, while the precipitation of iron oxide, being relatively rapid, is treated as an equilibrium reaction. The dissolution rate law for siderite is:

$$\frac{dm_s}{dt} = \left(k_s + k_{sb}a_{H^+}^{n_b}\right) \times m_s \times (1 - \Omega_s) \tag{1}$$

where  $dm_{s'}/dt$  is the overall rate of dissolution [moles second<sup>-1</sup>],  $k_{s}$  is the rate constant for the pH-independent dissolution mechanism [moles gram<sup>-1</sup> second<sup>-1</sup>],  $k_{sb}$  is the rate constant for the base-catalyzed dissolution mechanism [moles gram<sup>-1</sup> second<sup>-1</sup>],  $a_{H^+}$  is the proton activity (pH =  $-loga_{H^+}$ ), the exponent  $n_b$  is the order of the reaction mechanism with respect to proton activity,  $m_s$  [grams] is the mass of siderite in the system, and  $\Omega_s$  is the degree of saturation of porewater with respect to siderite.

Similarly, the rate law for calcite precipitation is:

$$\frac{dm_c}{dt} = k_c \times (\Omega_c - 1^{n_c}) \tag{2}$$

where  $dm_c/dt$  is the rate of calcite precipitation [moles second<sup>-1</sup>],  $k_c$  is the calcite precipitation rate constant (moles second<sup>-1</sup>),  $\Omega_c$  is the degree of saturation of porewater with respect to calcite, and  $n_c$  is an exponent relating the dependence of the reaction rate to the degree of saturation.

Kinetic rate constants for siderite dissolution and calcite precipitation were previously estimated by fitting of time series data from multiple kinetic batch tests carried out with granular siderite for a range of liquid-to-solid (L/S) ratios and grain size fractions (SSPA 2009). The results of the fitting were described in Parsons, 2011. No systematic trend between the fitted rate constants and grain size fractions was observed. This is explained by microscopic examination, which revealed that the granular siderite is an aggregate with individual particles much smaller than the smallest grain size fraction tested (0.125 - 0.25 mm). The geometric mean values of the experimentally derived rate constants were therefore used for the siderite and calcite kinetic rate constants in the model. These values are given in Table 1.

#### 3 Model Scenarios

Based on an evaluation of spatial variations in porewater pH and upwelling velocities, the following areas targeted for capping were selected for detailed cap pH modeling to determine appropriate area-specific siderite amendment rates:

- A2
- B1/C1 (combined)
- B2
- C2
- C3
- D-Center (ILWD)
- D-East (ILWD)
- D-West (ILWD)
- D-SMU2 (ILWD)
- Waste Beds 1-8
- Waste Bed B-Center
- Waste Bed B-West

For each of these twelve areas, the time-dependent porewater flux was represented as the sum of consolidation flux and groundwater upwelling. The porewater flux parameters are given in Table 2. Discussion on the development of upwelling velocities and consolidation curves used in the modeling are provided in Appendix C and Appendix E, respectively. The analytical cumulative porewater flux curves and their numerical model representations are compared in Figure 2. Note that the consolidation-induced porewater expression is essentially complete within 30 years. The 95<sup>th</sup> percentile values for porewater pH measured in each area (Appendix B) were used for the initial porewater pH. Initial pH values are

summarized in Table 2. The use of 95<sup>th</sup> percentile concentrations and mean upwelling velocities is consistent with the chemical isolation layer modeling presented in Appendix B. The transport, kinetic, and initial water chemistry parameters used for the twelve areas are summarized in Tables 1 and 2.

To estimate siderite dose requirements for the design cap lifetime of 1,000 years, long-term simulations were conducted for each area, First, an initial simulation was performed with the kinetic dissolution model with an excess of siderite in the pH amendment layer to obtain an initial rough estimate of the siderite dose. The total mass of siderite reacted after 1,000 years was determined and used as the initial siderite mass for a second iteration of the model. This was repeated until the total mass reacted changed by less than 2% between subsequent iterations. A total of five kinetic dissolution model iterations were run for each area to obtain final refined siderite dose estimates for.

The kinetic simulation results were also used to evaluate the initiation time to establish pH control within the cap for each model area. It was anticipated that initiation time would not be strongly affected by siderite dose but rather by the initial consolidation flux, which determines porewater residence time in the cap. This was confirmed by sensitivity runs.

#### 4 Model Results

Table 3 summarizes the model results for short-term pH excursions immediately following cap emplacement while Figures 3 through 14 display the short-term pH evolution curves for each of the twelve model areas. All the modeled areas exhibited short-term excursions of porewater pH (defined as pH greater than 8) in the chemical isolation layer and upper 3 inches of the pH amendment layer. For most of the modeled areas, the porewater pH excursions within the cap were generally dissipated within less than one year. The exceptions were areas B1/C1, B2, and Waste Beds 1-8 where the porewater pH excursions were generally dissipated within two years, due to a higher consolidation water flux than the other areas. Since pH neutralization reactions are kinetically controlled and depend on contact time, the extent of reaction is inversely related to porewater flux. During the initial stages of cap settlement, porewater pH may not be as effectively controlled in areas with higher consolidation porewater expression. However, these potential impacts are likely overestimated due to the intrinsic base-neutralizing property of the sand media, which was observed in the pH column tests with quarry sand, but is not accounted for in the cap pH

model. Increasing the siderite dose reduced the timeframe for pH excursions by 1-2 months, but did not suppress the elevated pH, even for a 100 percent siderite dose.

The siderite doses required in each model area to meet the long-term performance criteria of maintaining porewater pH below 8 in the cap above the mid-depth of the pH amendment layer for 1,000 years are summarized in Table 4. The kinetic simulations indicate that design value siderite mass application rates range from 1.68 to 5.65 weight percent. Figure 15 illustrates pH evolution curves at the mid-depth of the siderite-amended layer for all twelve model areas for the optimized siderite doses and kinetic dissolution.

#### 5 Sensitivity Analysis

A sensitivity analysis was conducted to assess the potential impact of non-uniform vertical distribution of siderite within the 6-inch pH amendment layer on short- and long-term cap effectiveness for porewater pH control. The higher grain density of siderite particles (3.74 g/cm<sup>3</sup>) relative to quartz sand (2.65 g/cm<sup>3</sup>) may result in partial segregation of siderite in the lower part of the 6-inch thick pH amendment layer during placement of the siderite-sand mixture.

Sensitivity of cap pH performance to non-uniform vertical distribution of siderite was evaluated for areas C2 and Waste Beds 1-8. These two areas were selected for sensitivity modeling based on high porewater pH values (12.2 and 12.4, respectively), upwelling velocities (3.05 and 1.10 cm/yr, respectively), and relatively higher calculated consolidation water fluxes than in other areas. The kinetic cap pH model with optimized siderite doses (Table 4) was used to conduct the sensitivity analysis.

Four scenarios with siderite segregated to varying degrees towards the bottom of the pH amendment layer were simulated for areas C2 and Waste Beds 1-8:

- 1) all siderite concentrated at the bottom of the pH amendment layer (lowermost model cell)
- 2) all siderite evenly distributed within the lower 1 inch of the pH amendment layer
- 3) all siderite evenly distributed within the lower 2 inches of the pH amendment layer, and
- 4) all siderite evenly distributed within the lower 3 inches of the pH amendment layer

The long-term cap pH performance criteria were met for all four siderite distribution scenarios using the Table 4 design doses. Figures 16 and 17 compare the porewater pH evolution curves at the mid-depth of the pH amendment layer (3 inches) for the original model scenario, with uniform siderite distribution across the pH amendment layer, to the four sensitivity model runs for areas C2 and Waste Beds 1-8, respectively. Based on these model results, long-term cap pH performance does not appear to be sensitive to variability in vertical distribution of siderite within the pH amendment layer.

The model results from the sensitivity analysis suggest that non-uniform siderite distribution may have some impact on the time to establish initial pH control within the cap. Nonuniform vertical siderite distribution resulted in a longer timeframe for initial pH control to be established within the cap in both model areas. Table 5 summarizes the sensitivity model results for time to establish pH less than 8 at all depths in the cap above the mid-point of the pH amendment layer and compares these to the original model scenario. Figures 18, 19, and 20 compare initial porewater pH evolution trends at mid-depth and top of the pH amendment layer and top of the chemical isolation layer, respectively, for uniform siderite distribution (throughout 6 inches) and the four sensitivity model runs for area C2 and Figures 21 to 23 show the same results for Waste Beds 1-8. As can be seen for area C2, the time to establish pH control within the cap is predicted to increase from approximately 6 months for uniform siderite distribution to a maximum of 12 months if all the siderite were to be concentrated at the bottom of the pH amendment layer. For Waste Beds 1-8, the time to establish pH control within the cap is predicted to increase from approximately 24 months to a maximum of 38 months if all the siderite were to be concentrated at the bottom of the pH amendment layer.

The vertical distribution of siderite within the pH amendment layer can impact the shortterm effectiveness of pH neutralization within the cap due to two competing factors affecting the kinetics of the siderite-porewater reaction:

 Shorter contact time of porewater with siderite (and potentially less than complete reaction) due to differential settling and segregation of siderite in the lower part of the pH Amendment Layer. This is expected to be more significant at early times immediately following cap placement, when porewater velocities are highest (and residence time lowest) due to consolidation water flux. 2) Higher reaction rates within the segregated zone due to the locally increased concentration (and therefore surface area) of siderite per unit pore volume, which may partially or completely compensate for the shorter contact time.

These potential impacts will likely be mitigated to some degree in the actual cap due to the intrinsic base-neutralizing property of the sand media, which was observed in the pH column tests with quarry sand, but is not accounted for in the cap pH model.

#### 6 Recommended Siderite Ore Dose by Cap Area

The recommended minimum doses of siderite ore to be applied in each of the twelve capping areas requiring pH amendment are presented in Table 4. The doses are calculated assuming an average siderite content for the raw ore of 74 % by weight.

## 7 References

- Parkhurst, D.L., and C.A.J. Appelo (1999) User's guide to PHREEQC (Version 2)-a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. USGS Water-Resource Investigation Report 99-4259, 312 pp.
- Parsons (2011) Draft Onondaga Lake Capping, Dredging and Habitat Intermediate Design Appendix I. Prepared for Honeywell.
- S.S. Papadopulos & Associates (2009) ILWD Porewater pH Neutralization Batch Studies. Memorandum dated September 22, 2009. Prepared for Parsons.

#### Attachments

Tables

Figures

Appendix A Model Input and Output Files and Supporting Information

	Parameter	Units	Cap <sup>1</sup>	Influent Porewater <sup>2</sup>	Onondaga Lake Water <sup>2</sup>
	Habitat Layer	cm (ft)	30 (1.0)		
Dimensions	Chemical Isolation Layer	cm (ft)	23 (0.75)		
	pH Amendment Layer	cm (ft)	15 (0.5)		
	Upwelling Velocity	cm/yr	see Table 2		
Flow and	Diffusivity	cm²/s	6.0 x 10 <sup>-6</sup>		
Transport	Dispersivity	cm	6.0		
	Porosity	-	0.4		
Rate Constants <sup>2,3</sup>	Siderite dissolution, neutral mechanism (k <sub>s</sub> )	mol/g/s	9.77 x 10 <sup>-12</sup>		
	Siderite dissolution, base- catalyzed mechanism, $(k_{sb})$	mol/g/s	5.55 x 10 <sup>-22</sup>		
	Calcite precipitation $(k_c)$	mol/s	6.75 x 10 <sup>-10</sup>		
	Temperature	°C	11.0	11.0	11.0
	рН	-	7.0	see Table 2	7.0
	Dissolved Oxygen	mg/L	1.5	0.	1.5
	Alkalinity	mg/L as CaCO₃	10.7	1,440	10.7
Water	Calcium	mg/L	59.2	5,780	59.2
Chemistry	Potassium	mg/L	4.2	282	4.2
	Magnesium	mg/L	22.8	0.	22.8
	Sodium	mg/L	193	8,460	193
	Chloride	mg/L	359	25,100	359
	Sulfate	mg/L	144	280	144

Table 1. Input Parameters for PHREEQC Cap pH Model

<sup>1</sup>Initial porewater in cap assumed to have chemical composition of lake water.

<sup>2</sup>Parsons 2011, Appendix I.

<sup>3</sup>Geometric mean of rate constants derived from fitting of granular siderite batch tests.

Cap Area	۲Ha	Upwelling Velocity <sup>2</sup>	Consolidation Water Flux <sup>3</sup>			
	•	cm/yr (ft/yr)	a (ft/yr <sup>b</sup> )	b		
A2	9.7	4.10 (0.135)	1.42	0.046		
B1/C1	12.3	1.02 (0.033)	2.08	0.046		
B2	12.2	0.51 (0.017)	2.25	0.046		
C2	12.2	3.05 (0.100)	1.73	0.108		
C3	10.0	1.50 (0.049)	1.73	0.108		
D-Center (ILWD)	12.3	0.68 (0.022)	0.31	0.226		
D-East (ILWD)	12.1	0.37 (0.012)	0.31	0.226		
D-SMU2 (ILWD)	11.8	1.53 (0.050)	0.31	0.226		
D-West (ILWD)	12.2	1.11 (0.036)	0.31	0.226		
Waste Bed 1-8	12.4	1.10 (0.036)	2.25	0.046		
Waste Bed B-Center	12.4	1.22 (0.040)	0.06	0.30		
Waste Bed B-West	12.4	1.73 (0.057)	0.06	0.30		

Table 2. Porewater pH and Flow Parameters for Modeled Cap Areas

<sup>1</sup>95<sup>th</sup> percentile value of porewater pH measurements in area (Appendix B).

<sup>2</sup>Mean value of measured porewater upwelling (Darcy) velocities in area (Appendix C).

<sup>3</sup>Cumulative Consolidation Water Flux (ft) =  $a \cdot t(yrs)^{b}$  (Appendix E).

	Time to pH <8 in:						
Cap Area	Habitat Layer <sup>2</sup>	Chemical Isolation Layer <sup>2</sup>	Upper 3 inches of Siderite Layer				
	months	months	months				
A2	1	1	1				
B1/C1	26	19	4				
B2	24	18	4				
C2	6	3	4				
C3	1	2	2				
D-Center (ILWD)	1	2	3				
D-East (ILWD)	1	2	2				
D-SMU2 (ILWD)	1	1	2				
D-West (ILWD)	1	2	2				
Waste Beds 1-8	24	19	5				
Waste Bed B-Center	<1	<1	1				
Waste Bed B-West	<1	<1	1				

Table 3. Estimated Time to Establish Initial pH Control in Capping Areas<sup>1</sup>

<sup>1</sup>Optimized siderite dose satisfying long-term criterion used for each cap area.

<sup>2</sup>These are upper bound estimates for the Habitat Layer and Chemical Isolation Layer. Actual time to establish initial pH control within the sand cap will likely be shorter than predicted due to the intrinsic buffering capacity of the quarry sand.

Cap Area	Siderite Do	osage <sup>1</sup>	Siderite Ore Dosage <sup>2</sup>			
	percent by weight <sup>3</sup>	lbs/sq ft⁴	percent by weight <sup>3</sup>	lbs/sq ft <sup>4</sup>		
A2	5.00	3.11	6.76	4.20		
B1/C1	2.52	1.57	3.41	2.12		
B2	1.92	1.20	2.60	1.62		
C2	5.65	3.51	7.63	4.75		
C3	2.11	1.31	2.85	1.77		
D-Center (ILWD)	2.08	1.29	2.81	1.75		
D-East (ILWD)	1.68	1.04	2.27	1.41		
D-SMU2 (ILWD)	2.75	1.71	3.71	2.31		
D-West (ILWD)	2.46	1.53	3.32	2.06		
Waste Beds 1-8	2.75	1.71	3.72	2.31		
Waste Bed B-Center	2.66	1.65	3.59	2.23		
Waste Bed B-West	3.32	2.07	4.49	2.79		

Table 4. Estimated Minimum Siderite Dosage for Capping Areas

<sup>1</sup>To maintain pH <8 in cap including upper half (top 3 inches) of pH amendment layer for cap lifetime of 1,000 years. Values are based on kinetic dissolution of siderite.

<sup>2</sup>Siderite ore dosage calculated assuming siderite ore contains an average of 74% siderite by weight. <sup>3</sup>In pH amendment layer

<sup>4</sup>Cap area

	Distribution of	Time to Establish pH <8 <sup>1</sup>					
Capping Area	Siderite in pH	Habitat Layer	Chemical Isolation Layer	Upper 3 inches of Siderite Layer			
	Amenument Layer	months	months	Months			
	All in lowest model cell	12	8	4			
	All in lower 1 inch	10	6	4			
C2	All in lower 2 inches	9	9 5				
	All in lower 3 inches	8	4	4			
	Uniform throughout 6 inches	6	3	4			
	All in lowest model cell	38	32	10			
	All in lower 1 inch	36	31	7			
Waste Beds 1-8	All in lower 2 inches	36	31	5			
	All in lower 3 inches	34	29	5			
	Uniform throughout 6 inches	24	19	5			

Table 5. Effect of Siderite Vertical Distribution on Estimated Time to Establish Initial pH Control

<sup>1</sup> These are upper bound estimates for the Habitat Layer and Chemical Isolation Layer. Actual time to establish initial pH control within the sand cap will likely be shorter than predicted due to the intrinsic buffering capacity of the quarry sand.



Figure 1. Conceptual model for Onondaga Lake sediment cap model.



Figure 2. Post-construction porewater flux curves for the different areas to be capped. Symbols: analytical expressions for cumulative upwelling and cap consolidation flux; solid lines: PHREEQC timestepping.



Figure 3. Simulated initial porewater pH evolution trends at mid-depth and top of siderite layer and top of GAC-amended chemical isolation layer for area ILWD D-East.



Figure 4. Simulated initial porewater pH evolution trends at mid-depth and top of siderite layer and top of GAC-amended chemical isolation layer for area ILWD D-Center.



Figure 5. Simulated initial porewater pH evolution trends at mid-depth and top of siderite layer and top of GAC-amended chemical isolation layer for area ILWD D-West.



Figure 6. Simulated initial porewater pH evolution trends at mid-depth and top of siderite layer and top of GAC-amended chemical isolation layer for area ILWD D-SMU2.



Figure 7. Simulated initial porewater pH evolution trends at mid-depth and top of siderite layer and top of GAC-amended chemical isolation layer for area A2.



Figure 8. Simulated initial porewater pH evolution trends at mid-depth and top of siderite layer and top of GAC-amended chemical isolation layer for area B2.



Figure 9. Simulated initial porewater pH evolution trends at mid-depth and top of siderite layer and top of GAC-amended chemical isolation layer for area C2.



Figure 10. Simulated initial porewater pH evolution trends at mid-depth and top of siderite layer and top of GAC-amended chemical isolation layer for area C3.



Figure 11. Simulated initial porewater pH evolution trends at mid-depth and top of siderite layer and top of GAC-amended chemical isolation layer for area B1/C1.



Figure 12. Simulated initial porewater pH evolution trends at mid-depth and top of siderite layer and top of GAC-amended chemical isolation layer for Waste Beds 1-8.



Figure 13. Simulated initial porewater pH evolution trends at mid-depth and top of siderite layer and top of GAC-amended chemical isolation layer for Waste Bed B-Center.



Figure 14. Simulated initial porewater pH evolution trends at mid-depth and top of siderite layer and top of GAC-amended chemical isolation layer for Waste Bed B-West.



Figure 15. Simulated porewater pH breakthrough curves at mid-depth (3 inches) of siderite layer in different cap areas based on kinetic siderite dissolution model.



16. Simulated porewater pH breakthrough curves at mid-depth (3 inches) of pH amendment layer for Remediation Area C2 with varying siderite distribution.



Figure 17. Simulated porewater pH breakthrough curves at mid-depth (3 inches) of pH amendment layer for Waste Beds 1-8 with varying siderite distribution.



Figure 18. Effect of siderite distribution on simulated initial porewater pH evolution trends at mid-depth of the pH amendment layer for area C2.



Figure 19. Effect of siderite distribution on simulated initial porewater pH evolution trends at the top of the pH amendment layer for area C2.



Figure 20. Effect of siderite distribution on simulated initial porewater pH evolution trends at the top of the chemical isolation layer for area C2.



Figure 21. Effect of siderite distribution on simulated initial porewater pH evolution trends at mid-depth of the pH amendment layer for Waste Beds 1-8.



Figure 22. Effect of siderite distribution on simulated initial porewater pH evolution trends at the top of the pH amendment layer for Waste Beds 1-8.



Figure 23. Effect of siderite distribution on initial porewater pH evolution trends at the top of the chemical isolation layer for Waste Beds 1-8.

#### ATTACHMENT A

# MODEL INPUT AND OUTPUT FILES AND SUPPORTING INFORMATION (CD)

#### ATTACHMENT A

# MODEL INPUT AND OUTPUT FILES AND SUPPORTING INFORMATION (CD)

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I.2

## SIDERITE LEACHATE EVALUATION

#### **APPENDIX I.2**

#### SIDERITE LEACHATE EVALUATION

Testing was conducted to evaluate potential water quality impacts during and after placement of siderite as part of an amended sediment cap. This included bulk chemical analyses for general characterization, modified elutriate testing (MET), and sequential batch leach testing (SBLT) (Parsons, 2009).

The MET evaluation was completed to evaluate potential impacts during material placement. Siderite was mixed with distilled/deionized water, and water samples were collected and analyzed following a 24-hour settlement period. The supernatant was analyzed for total and dissolved target analyte list (TAL) metals, semivolatiles (EPA Method 8260), total cyanide, hardness, pH, and total suspended solids. For dissolved concentrations, an aliquot of the supernatant was centrifuged prior to analysis.

Results from the MET testing (Parsons, 2009) verify that water quality impacts from siderite during cap placement will not be a concern. As shown in Table I.2-1, there were no exceedances of NYSDEC acute surface water quality criteria. Any impacts to water quality would be minor, localized and dissipate rapidly following material placement.

The SBLT was designed to evaluate leaching of constituents from siderite by upwelling porewater following cap placement. SBLT testing was conducted using porewater from the in-lake waste deposit (ILWD), which is the area where siderite is proposed in the initial design as part of the sediment cap. SBLT testing was completed on powered, pelletized and granular siderite. For each of the three forms of siderite ILWD porewater and siderite amendment were added to a container at a liquid to solid ratio of 4:1 and tumbled for 24 hours. The leachate was then removed by centrifugation and decanting. The porewater was replaced and the mixture placed on the tumbler for another 24 hours, after which the porewater was decanted again. This procedure was repeated for a total of four cycles. The initial porewater and leachates from each cycle were analyzed for TAL metals, semivolatiles, total cyanide, pH, and total suspended solids were also measured. Subsequent design evaluations indicate that the amended cap will use granular siderite. Therefore, the discussion below focuses on the results from the granular siderite testing.

SBLT test results verify that there would be no significant long-term impacts resulting from porewater migration through the siderite. Table I.2-2 compares the SBLT leachate analyte concentrations with the ILWD porewater in order to identify potential contributions from siderite. As shown in Table I.2-2, the majority of analytes were not detected or actually showed decreased concentrations in the leachate, perhaps as a result of precipitation, such as for mercury and vanadium. There were some metals, such as aluminum and zinc, which showed variability, or at most, potentially minor increases in comparison to the ILWD porewater. The only metal which showed consistently elevated concentrations in the leachate was approximately 6.4 ug/L, which only slightly

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exceeds the NYSDEC chronic surface water criteria of 5 ug/L. Any metals contribution to the cap porewater would be minor and would be quickly attenuated by the overlying sediment cap.

Semivolatile organic compounds were also analyzed for in the leachate, primarily to identify any impacts due to the manufacturing process associated with the pelletized siderite, which is no longer under consideration. Bis(2-ethylhexyl)phthalate (BEHP) was detected sporadically at low levels in the leachate from all forms of siderite. BEHP is a common laboratory or sample handling artifact. It is used as a plasticizer and may be derived from materials that the siderite samples were in contact with during shipping or sample processing. It would not be expected to be present in granular siderite.

#### REFERENCES

- Parsons, 2009. Onondaga Lake Pre-Design Investigation: Phase IV Work Plan Addendum 7 Cap pH Amendment Evaluation Addendum.
- Parsons, 2009. Onondaga Lake Pre-Design Investigation: Draft Phase IV Data Summary Report Appendix H Cap pH Amendment Study

http://www.dec.ny.gov/regs/4590.html

Table I.2-1
Modified Elutriate Test Results Compared to NYSDEC Class B/C Water Quality Standards

			Granul			
Daramatar	Unite	Elutriate				Acute
Parameter	Units	Blank <sup>1</sup>	Rep 1	Rep 2	Rep 3	Aquatic
						Standard
Metals						
Aluminum (dissolved)	ug/L	23.4 B	212 B	177 B	1,190	NS
Arsenic (dissolved)	ug/L	<2	<2	<2	<2.7	340
Beryllium (total)	ug/L	0.4 B	6.6 B	4.5 B	6.2	NS
Cadmium (dissolved)	ug/L	<0.21	<0.21	<0.21	0.19 J	15.7²
Chromium (dissolved)	ug/L	<1.1	<1.1	<1.1	2.1 J	1,580²
Cobalt (total)	ug/L	<0.4	173	119	107	NS
Copper (dissolved)	ug/L	<4.6	<4.6	<4.6	<2.7	43.5 <sup>2</sup>
Lead (dissolved)	ug/L	<1.7	<1.7	<1.7	<1.3	366²
Mercury (dissolved)	ug/L	<0.038	<0.038	<0.038	<0.038	1.4
Nickel (dissolved)	ug/L	<0.78	107 B	88.7 B	40.4 B	1,350²
Selenium (dissolved)	ug/L	<2.9	<2.9	<2.9	<1.6	NS
Silver (dissolved)	ug/L	<0.54	<0.54	<0.54	<0.68	NS
Thallium (total)	ug/L	<2.4	4 J	3.4 J	<2.4	NS
Vanadium (total)	ug/L	<1.9	549	353	632	NS
Zinc (dissolved)	ug/L	<3.1	212	183	32.6 B	337²
Semivolatiles						
2,4-Dichlorophenol	ug/L	<0.13	<0.13	<0.13	<0.13	NS
2,4-Dimethylphenol	ug/L	<0.077	<0.078	<0.076	<0.077	NS
2,4-Dinitrophenol	ug/L	<5.9	<6	<5.8	<5.8	NS
bis(2-Ethylhexyl) phthalate	ug/L	4.1 B	<0.45	<0.44	3 BJ	NS
Hexachlorobenzene	ug/L	<0.17	<0.18	<0.17	<0.17	NS
Hexachlorobutadiene	ug/L	<0.12	<0.11	<0.11	<0.11	NS
Hexachlorocyclopentadiene	ug/L	<0.11	<0.11	<0.11	<0.11	NS
Hexachloroethane	ug/L	<0.077	<0.074	<0.073	<0.072	NS
Pentachlorophenol	ug/L	<1.8	<1.8	<1.8	<1.8	10.5 <sup>2</sup>
Phenol	ug/L	<0.24	<0.23	<0.22	9.8	NS
Other						
Cyanide	ug/L	<1.5	<1.5	<1.5	<1.5	22
рН	su	5	5.3	5.4	5.7	NS

Notes:

1: Elutriate blank is DI water with a pH of 5

2: Water quality standard is pH and/or hardness dependent. Standard calculated using the lowest reported hardness (348 mg/L) and pH (7.18) from 2006 monitoring data, Onondaga Lake Ambient Monitoring Program

< - result is non-detect at the reported method detection limit (MDL)

J - estimated value, result is less than the reporting limit (RL) but greater than the MDL

B - analyte detected in associated laboratory blank

NS - no standard

#### ONONDAGA LAKE CAPPING, DREDGING, HABITAT AND PROFUNDAL ZONE (SMU 8) FINAL DESIGN

			Rep 1			Rep 2				
Daramatar	Unito	SBLT	Leach							
Parameter	Units	Solution <sup>1</sup>	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 1	Cycle 2	Cycle 3	Cycle 4
Metals										
Aluminum (dissolved)	ug/L	23.1 BJ	33.4 BJ	26.3 BJ	<9.7	20.6 J	46.6 BJ	26.3 BJ	<9.7	13 J
Arsenic (dissolved)	ug/L	13.6	6.2 J	7.4 J	5 J	8 J	5.8 J	7.4 J	8.7 J	5.8 J
Beryllium (total)	ug/L	0.8 J	0.75 J	1.1 J	0.83 J	0.65 J	0.75 J	1.1 J	0.89 J	0.69 J
Cadmium (dissolved)	ug/L	<0.13	<0.13	<0.13	<0.13	<0.13	1.1 J	<0.13	<0.13	<0.13
Chromium (dissolved)	ug/L	<0.57	0.67 J	1.6 J	1.6 J	5.3	1.3 J	0.94 J	1.2 J	2.6 J
Cobalt (total)	ug/L	1.5 J	15.9 J	4.6 J	2.7 J	3.2 J	13.2 J	4.6 J	3.5 J	3.4 J
Copper (dissolved)	ug/L	<2.7	3.8 J	4.8 J	<2.7	12.3 J	5.7 J	4.8 J	<2.7	<2.7
Lead (dissolved)	ug/L	<6.3	<6.3	<6.3	<6.3	<6.3	<6.3	<6.3	<6.3	<6.3
Mercury (dissolved)	ug/L	26.2	<0.038	<0.038	0.046 J	0.095 J	<0.038	<0.038	0.048 J	0.076 J
Nickel (dissolved)	ug/L	167	245	248	200	185	268	243	206	181
Selenium (dissolved)	ug/L	5.7	8.1	8.5	6.1	6.2	7.5	5.2	6.6	3.7 J
Silver (dissolved)	ug/L	<0.68	<0.68	<0.68	<0.68	<0.68	<0.68	<0.68	<0.68	<0.68
Thallium (total)	ug/L	<2.4	<2.4	<2.4	<2.4	<2.4	<2.4	<2.4	<2.4	<2.4
Vanadium (total)	ug/L	2.2 J	<1.9	<1.9	<1.9	<1.9	2.9 J	<1.9	<1.9	<1.9
Zinc (dissolved)	ug/L	11.4 BJ	11.7 BJ	24 BJ	30.3 B	41.4 J	22.9 B	13.7 BJ	13.8 BJ	12 BJ
Semivolatiles										
2,4-Dichlorophenol	ug/L	<0.2	<0.24	<0.19	<0.24	<0.21	<0.21	<0.19	<0.24	<0.2
2,4-Dimethylphenol	ug/L	7 J	3.7 J	6.6 J	7.1 J	8 J	3.4 J	6.4 J	0.9 J	8.7 J
2,4-Dinitrophenol	ug/L	<9.1	<11	<8.8	<11	<9.8	<9.5	<8.8	<11	<9
bis(2-Ethylhexyl) phthalate	ug/L	<0.69	7.1 J	5.6 J	<0.81	6.6 J	6.3 J	5.6 J	<0.81	5.6 J
Hexachlorobenzene	ug/L	<0.27	<0.32	<0.26	<0.32	<0.29	<0.28	<0.26	<0.32	<0.27
Hexachlorobutadiene	ug/L	<0.18	<0.21	<0.17	<0.21	<0.21	<0.19	<0.17	<0.21	<0.21
Hexachlorocyclopentadiene	ug/L	<0.17	<0.2	<0.16	<0.2	<0.18	<0.18	<0.16	<0.2	<0.17
Hexachloroethane	ug/L	<0.11	<0.13	<0.11	<0.13	<0.12	<0.12	<0.11	<0.13	<0.11
Pentachlorophenol	ug/L	<2.8	<2.9	<2.7	<3.3	<3	<2.8	<2.7	<3.3	<2.8
Phenol	ug/L	520	420	570 J*	520	580	410	540	71	650
Other										
Total Cyanide	ug/L	696	135	28.7	22.8	36	136	19.4	11.5	32.6
рН	s.u.	11.8	8.1	7.1	6.8	7.4	8.2	7.2	7.4	7.1

#### Table I.2-2

#### Sequential Batch Leach Test Results for Granular Siderite (Sidco)

Notes:

1: SBLT blank solution is porewater collected from location TR-03A.

< - result is non-detect at the reported method detection limit (MDL)

J - estimated value, result is less than the reporting limit (RL) but greater than the MDL

B - analyte detected in associated laboratory blank

#### **I.2**

#### SIDERITE LEACHATE EVALUATION