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May 27, 2010

Mr. Timothy Larson
Project Manager
New York State Department of Environmental Conservation
Division of Environmental Remediation
Remedial Bureau D
625 Broadway, 12th Floor
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**RE: Onondaga Lake Bottom Subsite – Onondaga County, New York
Consent Decree 89-CV-815
Pre-Design Investigation Phase VI Addendum 2 pH Column Studies Work Plan
Action Item Cap-30i**

Dear Mr. Larson:

This letter presents the pH Column Studies Work Plan. This letter provides the proposed scope of work and details for the collection of additional data to support the design of an isolation cap.

1.0 INTRODUCTION

This memorandum serves as a work plan for pre-design column studies for a siderite-amended sediment cap to neutralize hyperalkaline porewater discharging through in-lake waste deposits (ILWD) at Onondaga Lake. Previous pre-design work included laboratory batch testing and cap pH modeling to determine performance characteristics and a minimum required mass application rate of siderite to meet both long-term and short-term cap pH neutralization effectiveness. The primary purpose of the proposed work is to provide information on potential porous media effects that need to be considered in up-scaling from bench scale to field scale.

1.1 Background

The Onondaga Lake sediment cap conceptual design incorporates biodegradation of organic contaminants occurring within the cap. Pre-design laboratory experiments conducted at the University of Texas using sediment slurries from SMU 1 indicated limited evidence for biodegradation, in contrast to sediment from other parts of the lake bed intended for capping. The sediment in SMU 1 contains hyperalkaline ILWD with porewater pH ranging from 9 to 12 (Parsons, 2009).

Previous work conducted by S.S. Papadopoulos & Associates (SSPA) determined that the hyperalkaline porewater pH (>11) is due to calcium-aluminum sulfate and silicate phases present in ILWD (SSPA, 2008). SSPA (2009a) subsequently evaluated several amendments for neutralizing pH in laboratory batch tests. Siderite (FeCO_3) was identified as the most suitable additive for pH control within the proposed sediment cap, and reaction rates were determined from the batch tests.

The laboratory testing was supplemented by sediment cap modeling using the geochemical reactive transport model PHREEQC (SSPA, 2009b) that evaluated minimum siderite mass application rates required. The model accounts for macroscopic porewater advection, molecular diffusion, and the rate of pH neutralization due to dissolution of siderite (calibrated to batch test results). Modeling results indicate that long-term porewater pH control could be achieved with a relatively low siderite mass application rate (equivalent to 2% siderite by weight in a 6-inch cap). One potential limitation of extrapolating the geochemical cap model predictions to the field scale is that the macroscopic fluid flow representation used in modeling to date does not explicitly account for transport at the pore scale. At low mass amendment rates, less siderite than the bulk average may be encountered along some porewater flow paths such that pH neutralization under field conditions may be less complete than predicted. In practice, this effect could be corrected by using a higher siderite application rate, however, it is presently difficult to evaluate a priori whether pore scale effects will be important at the recommended 2 percent mass application rate. The simplest and most reliable way to perform this evaluation is through column testing.

1.2 Objectives

The column studies described in this work plan are designed to simulate porewater pH neutralization within the amended cap under conditions more representative of the field. These results will be used to confirm geochemical model predictions of amended cap performance, and if necessary, provide a basis for revising the model and estimate of the minimum required siderite application rate in the cap amendment layer.

2.0 MATERIALS AND METHODS

Columns will be constructed with a siderite amendment sand layer emplaced between two layers of sand. The siderite amended layer will be either 3 or 6 inches thick, and siderite application rates will vary in individual columns from 2 to 10 percent by weight. Hyperalkaline porewater will be pumped through the columns in upflow mode at a flow rate expected to provide complete pH neutralization within the pore volume of the amendment layer, and pH will be monitored periodically.

2.1 Materials

Granular siderite will be obtained from Sidco Minerals. The bulk material will be screened to determine the grain size distribution, and the 1-2 mm size fraction will be retained for use in the column tests. Prior to use, the siderite will be rinsed with distilled water to remove extremely fine-grained material adhering to the larger grains. These fines were previously found to be more reactive than the bulk material due to their greater surface area, but are not likely to be retained during placement of the cap, therefore, are not expected to contribute to long-term pH neutralization in the cap.

Sand similar to the material expected to be used for cap construction will be obtained from a source provided by Parsons. Sand will be rinsed with distilled water prior to use to remove any extremely fine-grained material that would be removed during placement of cap materials in the lake.

Bulk water samples for the column study will be collected from an existing groundwater upwelling pump in Remediation Area D in accordance with SOP 16 (Parsons, 2005). Upwelling location TR05-B was selected as the most viable location because of its proximity to the shoreline, the integrity of the apparatus, the pH and the DOC content of the porewater. Location TR05-B will be purged and then sampled over a two to three-day time period to obtain approximately 25 gallons of porewater. The water will be pumped into 3.5-gallon containers and shipped to S.S. Papadopolous. The pH of the porewater will be tested periodically to ensure stability over the duration of the tests. The porewater will be sparged with air-free nitrogen and stored in a closed reservoir under a nitrogen atmosphere to maintain an anaerobic condition. A limited set of batch slurry experiments will be conducted in accordance with the procedures specified in the previous report (SSPa, 2009a). The batch tests will be used to derive pH neutralization rates for the specific grain-size distribution of siderite used in the columns, and as a further check for any variability in rate due to differences in porewater chemistry. Results from batch testing on the porewater from location TR-05B will be compared to the results of the previous testing, conducted on porewater from TR-03A, to identify any potential differences in waters from different locations.

2.2 Column Setup

The columns are constructed of 8-inch diameter cast acrylic with multiple sealed sampling ports along the length to allow measurement of pH profiles within the siderite amended layer, as well as in the adjacent sand layers. To ensure uniform flow across the amendment layer, columns will be packed from bottom up with sand, followed by the amendment layer (3 or 6 inches deep), and an additional layer of sand. The placement of a layer of sand above and below the amended layer will ensure that flow is diffuse entering and departing the amended layer, i.e. that flow within the amended layer is equal at the edges and the center and not affected by the convergence of flow experienced near the influent/effluent. The columns will be equipped with multiple ports along their entire length at approximately 1-inch spacing, which allows for multiple pH monitoring locations within the siderite amended layer, as well as in the adjacent sand layers. The columns will initially be filled with distilled water to facilitate packing of the bed material.

A multichannel pump will be used to supply porewater to all columns at the same flow rate.

Eight (8) columns will be set up to cover a range of siderite application rates and amendment layer thicknesses as follows:

- Three columns containing a 6-inch deep lower sand layer, a 3-inch deep siderite amended layer with application rates of 2 percent, 5 percent, and 10 percent by weight, and a 9-inch deep upper sand layer.
- Three columns containing a 6-inch deep lower sand layer, a 6-inch deep siderite amended layer with application rates of 2 percent, 5 percent, and 10 percent by weight, and a 6-inch deep upper sand layer.
- One replicate column (6-inch siderite amended layer at 5 percent application rate).
- One control column, containing 18 inches of sand.

2.3 Column Characterization

During assembly, the pore volume of each column will be determined by water displacement. Prior to testing, media hydraulic and transport characteristics (i.e. conductivity and dispersivity) will also be estimated using head loss measurements and salt tracer tests. Head loss will be measured using micro-piezometer tubes connected through ports at the bottom and top of the columns. A pumping rate will be used such that the measured head difference across the column is large enough that a change in head loss before and after column testing of at least 10 percent would be measurable. Tracer testing will be conducted using a sodium chloride tracer solution of comparable salinity to the porewater. Breakthrough curves will be measured using an inline conductivity probe (with automated datalogger) attached directly to the effluent end of the column. The pump rate will be set such that the retention time in the column will be approximately 30 minutes. Porosity and dispersivity will be estimated for each column by fitting the measured tracer breakthrough curves to the 1-D advection-dispersion equation. Although not anticipated to be an issue, head loss measurements will be repeated periodically to monitor for potential clogging of the column media by comparing with the baseline head loss data. Should head loss data indicate clogging is occurring, tracer tests may be repeated at the end of the column tests to evaluate whether development of preferential flow pathways may have impacted the column test results.

2.4 Column Operation

Prior to initiating the column tests, several pore volumes of porewater will be pumped rapidly through the columns to flush out residual tracer test fluid and set the initial condition for the pH testing. The porewater will be pumped from a large closed reservoir that will be continuously sparged with nitrogen to maintain anaerobic conditions. The flow rate will then be adjusted to achieve the minimum expected residence time needed to lower porewater pH to 8 at the lowest application rate (2 weight percent), estimated to be approximately 70 days based on interpolation of results of batch tests GS7 and GS8 (SSPA, 2009b). This 70-day period is much shorter than the expected porewater residence time within the siderite layer in the sediment cap (minimum of three years, based on porewater advection rates of 2 cm/yr or less). If pH monitoring data indicates that neutralization is occurring faster than expected, then the flow rate may be increased to shorten the duration of the column tests. The column tests will be operated for a minimum of 1.5 pore volumes to evaluate pH neutralization and may be extended to several pore volumes if initial data indicate that higher flow rates can be used.

3.0 ANALYSIS

Column influent and effluent solutions will be monitored for pH, specific conductance, oxidation-reduction potential (ORP), and dissolved oxygen (DO) on a weekly basis using appropriately calibrated probes. In addition, column pH profiles will also be measured at the start of the tests, at week 1, week 2, and every two weeks thereafter. pH profiles will be measured across the amended layer (multiple sampling ports are available within the amended layer) and will extend into the adjacent sand layers for 6 inches on either side of the amended layer. Samples for influent monitoring will be collected directly from the influent pump tubing through a syringe port.

Sampling and analysis of column effluents may also be conducted periodically for major ions, alkalinity, iron, and silica concentrations, if pH neutralization is not observed to proceed as expected. Alkalinity will be measured by titration and iron and silica will be determined using a Hach spectrophotometer. Samples for major ion analyses will be appropriately preserved and sent to TestAmerica under chain-of-custody for analysis.

If significant clogging is indicated by head loss measurements, selected column media will be characterized for mineralogy using XRD and SEM methods on completion of column testing to identify any secondary precipitates.

4.0 QUALITY ASSURANCE/QUALITY CONTROL

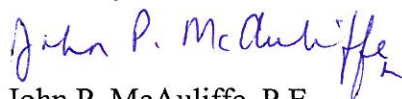
All analytical data will be collected in accordance with the Onondaga Lake Quality Assurance Project Plan as Level III data and will not undergo formal data validation. The data will be evaluated by the project manager as to its consistency with site conditions and developed conceptual models to determine whether the analytical data meets the requirements for decision making.

5.0 REPORTING

The results of the column study will be summarized in a technical memorandum. This will include (1) all the data generated as described above, (2) a description of any deviations from this work plan and (3) an evaluation of the results.

Please feel free to contact Caryn Kiehl-Simpson at 315-552-9702 or me if you have any questions.

Sincerely,



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