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ENVIRONMENT

Subject:

Technical Memorandum #1 – Summary of Nano-Scale Revised Nano-Scale Zero Valent Iron (nZVI) Kinetic and Phase II Field Testing Work Plan Activities, Phoenix-Goodyear Airport-North Superfund Site Goodyear, Arizona

Date:
August 3, 2007

Dear Ms. Aycock:

Contact:
Robert Ellis, LG

ARCADIS G&M, Inc. (ARCADIS), on behalf of Crane Co. has prepared this Technical Memorandum #1 to summarize activities related to the Revised Nano-Scale Zero Valent Iron (nZVI) Kinetic and Phase II Field Testing Work Plan (Work Plan). Activities completed to date include: 1) performance of two of three planned baseline groundwater sampling events; 2) development and testing of a batch kinetic testing protocol; 3) development and testing of a particle settling protocol; 4) development and performance of a 30-day nZVI batch shelf-life test; 5) evaluation of a procedure for de-aeration of water to be used for injections; and 6) commencement of kinetics testing. The following sections provide details and results for the sampling and testing activities performed to date, as well as an updated project and reporting schedule.

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1 Baseline Groundwater Sampling

Two of the three baseline events planned to occur prior to initiation of the Phase II nZVI injection have been performed as described in Section 6 of the Work Plan. The first two baseline sampling events included collection of groundwater samples from Main Drywells Area monitoring wells MW-A, MW-B, MW-C, and MW-D and were performed in November 2006 and January 2007, respectively. The third baseline sampling event will be performed after the proposed new Phase II field test injection wells are installed and developed during September 2007. A summary of baseline sampling and analyses program is provided in Table 1. The nZVI field pilot test monitoring well network is illustrated in Figure 1.

Groundwater sampling activities were conducted in accordance with the US EPA approved Groundwater Monitoring Quality Assurance Project Plan (QAPP). The

sampling intervals were determined from vertical stratification profiling performed in previous sampling activities. Low flow sampling was used to collect samples from the targeted intervals. A two-inch submersible pump was used and it was decontaminated prior to and after the sampling of each well.

Tables 2 through 4 provide a summary of data for the first two baseline sampling events as well as data for groundwater samples collected from upgradient monitoring well MW-01. Analytical results for inorganic compounds and target constituents (including field parameters, major cations, major anions, and trichloroethene [TCE]) are similar for samples collected during each of the first two baseline sampling events. Concentrations of inorganic compounds and target constituents are generally within the range historical concentrations detected in the Main Drywells Area, which indicates limited variability in water chemistry over time (See Tables 2 through 4).

In addition, water chemistry changes resulting from previous tracer tests and the previous nZVI injection events appear to have dissipated with time as groundwater has flowed through the Main Drywells Area. For example, bromide concentrations (used as a tracer during previous injections) appear to have returned to pre-injection concentrations in downgradient monitoring well MW-C (62 milligrams per liter [mg/L] on in January 2006 vs. 1.9 mg/L in January 2007). In addition, dissolved (ferrous) iron concentrations in downgradient monitoring well MW-C (18 mg/L in January 2006 vs. <0.5 mg/L in January 2007) appear to have also returned to background concentrations for this well.

Groundwater data for samples collected from MW-01 in May 2007 are also presented in Tables 2 through 4. Groundwater from MW-01 was selected for use during the kinetic testing because the water chemistry (major cations and anions, as well as, specific conductivity) are similar to those in monitoring wells MW-A through MW-D (See Tables 2 and 3). In addition, the TCE concentrations have historically been low (4.2 microgram per liter [$\mu\text{g/L}$] in May 2007, See Table 4), which allows the water from MW-01 for control samples during the kinetic testing. During the kinetic testing, water from MW-01 will be spiked with TCE as described in Section 4.2 of the Work Plan.

2 nZVI Bench Scale Testing

A series of laboratory tests is underway to evaluate the performance of newly formulated Polyflon PolymetallixTM nZVI (product number NSPP-GAM2M). Prior to performance of the kinetics testing specified in Section 4.2 of the Work Plan, preliminary testing has been performed.

2.1 ZVI Batch Testing SOP Development and Testing

A technical protocol for nZVI batch testing has been developed. The batch testing included adding a known mass of nZVI to a known volume of fluid with a TCE at a known concentration. The SOP was prepared submitted to EPA for review and comment on February 22, 2007, and approval to proceed with bench testing using the SOP was received on March 12, 2007. A copy of the standard operating procedure (SOP) for batch testing is provided in Attachment 1. The batch testing SOP was developed to be used during the shelf life testing (as described below) and will be used during the kinetic testing specified in Section 4.2 of the Workplan.

2.2 Particle Settling Test Protocol Development

A technical protocol to assess nZVI particle settling velocity has been developed. This settling test protocol was not designed to quantify particle size distribution, but rather is intended to be used as a quick screening tool to evaluate significant changes in particle settling behavior, which can be interpreted to indicate major changes in particle size distribution. The SOP was prepared submitted to EPA for review and comment on February 22, 2007, and approval to proceed with bench testing using the SOP was received on March 12, 2007. A copy of the USEPA-approved SOP for particle settling is provided in Attachment 1. The particle settling SOP was developed to be used during the shelf life testing (as described below) and will be used during the planned kinetic testing.

2.3 Shelf Life-Testing

To evaluate potential loss of reactivity during the short time frame anticipated between manufacturing and injection, a 30-day nZVI batch shelf-life reactivity test was performed in May and June 2007. The SOP was prepared submitted to EPA for review and comment on February 22, 2007, and approval to proceed with bench testing using the SOP was received on March 12, 2007. A copy of the USEPA-approved SOP for shelf life testing is provided in Attachment 1. For the test, one fresh batch of 30 grams per liter [g/L] nZVI was prepared on May 7, 2007, and split into two aliquots for use during the longevity testing. A dispersing agent, sodium hexametaphosphate (SHMP), was added at a concentration of 10% by weight to one of the nZVI aliquots. The second aliquot was not amended. Water used during the longevity testing for preparation of TCE stock solutions and sample preparation was de-oxygenated to <0.5 mg/L by sparging with nitrogen, similar to the process described below in Section 2.4.

A total of six batch reactivity tests (following the SOP in Attachment 1) were performed periodically during the longevity testing period as the nZVI "aged". While the nZVI "aged", it was stored in unvented bottles on the laboratory shelf. The time frame between tests was generally five days, but a few adjustments were made to avoid the need for setup or lab analyses on weekends and holidays.

During each test, a fresh TCE stock solution was prepared as per the SOP. Sample "blanks" were set up and analyzed in triplicate to establish a starting concentration for the reactivity test treatments. Each nZVI treatment (nZVI-only and nZVI+10%SHMP) were set up and analyzed in duplicate. A summary of the longevity testing results is presented in Table 5 and the associated laboratory reports are presented in Attachment 2.

Laboratory analyses for the first five batch tests during the longevity testing yielded elevated reporting limits due to the applied dilution factor. However, even with the reporting limits, the results indicate a greater than 98% reduction of significant concentration of TCE, by both nZVI and nZVI+10% SHMP treated samples up to 29 days after the fresh batch of nZVI was prepared (See Table 5).

In addition, the project team requested lower reporting limits for the final batch reactivity test (Test #6), which was initiated after the nZVI had aged for 36 days. Results for the final batch reactivity test indicate that TCE concentrations were not detected above 5µg/L, which equates to a 99.95% reduction in TCE concentrations. These data demonstrate adequate and reliable TCE destruction by both nZVI types over the course of the longevity testing period.

A summary of nZVI particle settling behavior over the course of the longevity testing, as interpreted using the particle settling SOP (Attachment 1) is presented in Table 6. Again, the settling test protocol was not designed to quantify particle size distribution, but rather is intended to be used as a cost effective and quick screening tool to evaluate significant changes in particle settling behavior, which can be interpreted to indicate major changes in particle size distribution. As presented in Table 6, the nZVI particle settling behavior did not change more than +/- 10% over the course of the longevity test for both nZVI and nZVI+10% SHMP material, which suggests that the particle size distribution did not change significantly over a period of 30 days.

Academic literature and ARCADIS' experience indicates that nZVI particles undergo minor physiochemical changes beginning immediately after their preparation. However, the batch reactivity testing results and particle settling behavior observed over the course of the longevity testing described herein, suggests little or no

significant changes that would affect the reactivity and/or particle size of Polyflon Polymetallix™ nZVI over a period of 36 days. Actual timeframe between production, shipment, and injection is expected to be within 8 to 10 days for the planned Phase II field injection test.

2.4 Nitrogen Purge Evaluation

The ARCADIS Treatability Lab performed a short-term tank study to determine the time and volume nitrogen necessary to reduce the dissolved oxygen (DO) of a 100 gallon tank to less than 1 mg/L. The purpose of the tank study was to evaluate the use of nitrogen to remove dissolved oxygen (DO) from water as a possible alternative to the approach discussed in the work plan (ZVI) for use during the preparation, mixing, and injection of nZVI. Removal of DO will reduce the potential for non-target corrosion (oxidation) of nZVI particles prior to injection.

2.4.1 Materials and Methods

A 130 gallon capacity tank was filled with 117 gallons of tap water leaving a 13 gallon headspace. The tank was sparged with nitrogen gas at a regular rate of 2.5 liters/minute through a large aquarium air stone (Bubble Disc Airstone – 5 inch diameter) over a 21 hour period. The DO concentration in water within the tank was assayed at regular intervals (see Table 1) with a dissolved oxygen test kit (Chemetrics - Indigo Carmine Method, 1-12 mg/L or Rhodazine D Method, 0-1 mg/L). To determine the DO concentrations of the water within the tank water, water was sampled through a tap installed at the bottom of the tank.

Table 1: DO Level and Nitrogen Consumption Data.

Elapsed Time (Hr:Min)	Nitrogen flow (liters/minute)	Total Nitrogen used (liters)	Nitrogen Used Per Gallon of Water Sparged (liters)	DO (mg/L)
1:35	0	0	0	8
2:05	2.5	237.5	2.0	3

