

REVISED CO₂ NEUTRALIZATION PILOT STUDY WORK PLAN

Former Rhone-Poulenc Site
Tukwila, Washington

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January 2017

Project No. 0087690050.00010.****



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By: 
Mr. Gary Dupuy, Project Coordinator

Date: January 13, 2017

TABLE OF CONTENTS

	Page
1.0 INTRODUCTION	1
1.1 STATEMENT OF THE PROBLEM	1
1.2 HIGH PH TARGET AREA CONDITIONS	2
1.2.1 Hydrogeologic Conditions	2
1.2.1.1 HCIM Area	2
1.2.1.2 Shoreline Area	3
1.2.2 Groundwater Chemistry Data	3
2.0 CHEMICAL EQUILIBRIUM MODELING	5
2.1 METHODS.....	5
2.2 GROUNDWATER CHEMISTRY MODELING RESULTS	6
3.0 PILOT STUDY OBJECTIVES.....	9
3.1 INITIAL CO ₂ CONSUMPTION ASSESSMENT	10
3.2 CO ₂ INJECTION RATES AND INJECTION PRESSURES.....	10
3.3 RADIUS OF INFLUENCE.....	11
3.4 GROUNDWATER MOUNDING	11
3.5 ASSESSMENT OF PH NEUTRALIZATION AND REBOUND RATES	12
3.6 CO ₂ UTILIZATION EFFICIENCY AND CONSUMPTION.....	12
3.7 CHANGES IN AQUIFER CHARACTERISTICS.....	13
3.8 CHANGES IN GROUNDWATER AND SOIL CHEMISTRY	13
4.0 PILOT STUDY METHODS	15
4.1 AQUIFER SLUG TESTING	17
4.2 CO ₂ INJECTION, OBSERVATION, AND VENT WELL DETAILS	18
4.2.1 CO ₂ Injection Well	19
4.2.2 Observation Wells	20
4.2.3 Vent Well.....	21
4.2.4 Well Construction Details	21
4.3 BENCH SCALE STUDIES	23
4.3.1 Groundwater Chemistry Bench Study.....	23
4.3.2 Soil Buffering Capacity Study	24
4.4 FIELD PILOT STUDY TESTING AND MONITORING PLAN.....	28
4.4.1 Phase 1 Testing: Evaluation of Injection Pressure and Flow Rates.....	30
4.4.2 Phase 2 Testing: pH and Water Chemistry Monitoring	32
4.4.3 Phase 3 Testing: Full-Scale Injection Simulation	33
4.4.4 Phase 4 Testing: Rebound Monitoring.....	35
4.5 PROTECTIVENESS MONITORING	36
4.6 SAMPLING	36
4.7 PERMITTING	36
5.0 REPORTING	39
6.0 SCHEDULE	41
7.0 REFERENCES	43



TABLE OF CONTENTS (Continued)

TABLES

Table 1	Groundwater pH Measurements
Table 2	Pilot Study Wells pH, Total Alkalinity, and Total Dissolved Silicon
Table 3	Performance Monitoring Round 28 Water Chemistry Data
Table 4	CO ₂ Pilot Study Data Quality Objectives
Table 5	CO ₂ Injection Field Study Monitoring Plan
Table 6	Pilot Study Area and High pH Shoreline Area Well Details

FIGURES

Figure 1	Approximate Extent of High pH Areas
Figure 2	Duwamish and Slip 6 Shoreline Cross Section pH Contamination Summary
Figure 3	MW-44 pH and Silicon Trend Data
Figure 4	Total SiO ₂ vs pH in Shoreline Area Groundwater
Figure 5	Predicted Total CO ₂ Required to Reduce pH in Shoreline Area Groundwater
Figure 6	Pilot Study Monitoring and Injection Well Layout
Figure 7	CO ₂ Pilot Study Cross Section C-C'

DRAWINGS

Drawing 1	Proposed Pilot Study Well Details
Drawing P&ID 01	CO ₂ Injection System Process and Instrumentation Diagram

ATTACHMENTS

Attachment A	Calculations for CO ₂ Injection Pressures
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REVISED CO₂ NEUTRALIZATION PILOT STUDY WORK PLAN

Former Rhone-Poulenc Site Tukwila, Washington

1.0 INTRODUCTION

The former Rhone-Poulenc facility (site) is located adjacent to the Duwamish Waterway in Tukwila, Washington. This CO₂ Neutralization Pilot Study Work Plan (work plan) was prepared to document plans for performing a pilot study to assess the injection of CO₂ to neutralize portions of the site with soil and groundwater exhibiting high pH. Results from the pilot study will be used to complete the Corrective Measures Study (CMS) that is being performed to address the requirements of the Resource Conservation and Recovery Act (RCRA) Administrative Order on Consent (Order) No. 1091-11-20-3008(h). The draft CMS Work Plan (AMEC, 2014) includes a preliminary screening of remedial technologies to be included in the CMS for the site. The preliminary technology screening identified CO₂ injection as the preferred technology for neutralizing groundwater affected by high pH in the Shoreline Area. This technology has had a limited history of use; site-specific testing is needed to fully assess its applicability and to collect the detailed information needed to evaluate CO₂ injection as a component of the corrective measures alternatives.

This work plan documents the objectives, testing plan, and monitoring plan for performing a pilot study that will assist in the technical and cost evaluation of using CO₂ to neutralize high pH soil and groundwater. The high pH target area lies in the Shoreline Area, which is located between the hydraulic control interim measure (HCIM) Area barrier wall and the Duwamish Waterway and Slip 6 (Figure 1). The pH-affected area was a result of historical releases of sodium hydroxide from a storage tank that was located near the southwest corner of the site. Due to potential adverse effects to the adjacent surface water and site workers that could be caused by injection of acid, CO₂ was selected as the preferred pH neutralizer, because the acidic gas would have limited effect on surface water and site workers if releases occurred during injection. In addition, the pilot study will be performed inside the barrier wall to limit potential adverse effects while performing the study. The pilot study area is shown on Figure 1.

1.1 STATEMENT OF THE PROBLEM

As discussed in Section 3 of the CMS Work Plan, elevated pH levels have been observed in groundwater in the southwest portion of the site, both inside and outside the barrier wall. The high pH area lies within the pH 8.5 contour in the Shoreline Area (Figure 1). The vertical extent of pH contamination is shown on the cross sections provided in Figure 2, based on the maximum pH values



observed during site groundwater monitoring from March 2008 to present, and data from the 2011 shoreline investigation. These data are also summarized in Table 1. The maximum pH measurement shown on Figure 1 and Table 1 is 11.50, measured in push probe SL-12, in the Shoreline Area along Slip 6 west of the MW-43/44 well cluster. Historical sample locations and data collected prior to 2008 are also shown on Figure 1. The contoured data on Figure 1 show that the area of elevated groundwater pH values is limited to the southwest corner of the site and includes a portion of both the HCIM and Shoreline Areas. This figure also shows that pH levels elsewhere on the site are near neutral and slightly acidic, as normally observed for groundwater in this area. As discussed in the CMS Work Plan, the pH levels tend to be highest at depths ranging from approximately 30 to 60 feet below ground surface (bgs).

High pH groundwater and soil located inside the HCIM Area wall have been effectively isolated from the environment and have limited potential to cause adverse impacts on human health and the environment for as long as the HCIM is in place and functional. The area of elevated pH located in the Shoreline Area along Slip 6 and the Duwamish Waterway is not contained, and high pH groundwater may be released to the nearby surface water. The high pH area to be addressed in the CMS lies within the pH 8.5 contour within the Shoreline Area (Figure 1); this area is defined as the high pH target area. A pH of 8.5 was selected based on the Washington State Department of Ecology surface water quality criteria for the Duwamish Waterway. Other contaminants are present in the high pH target area at concentrations exceeding their preliminary remediation goals (PRGs); neutralization of the high pH may be necessary to successfully remediate the other constituents of concern (COCs) in this area, particularly copper and other metals.

1.2 HIGH PH TARGET AREA CONDITIONS

Site characterization work conducted to date is discussed in Sections 2 and 3 of the CMS Work Plan. The hydrogeologic conditions that affect the high pH target area are briefly described below, along with a summary of groundwater results for pH and other important groundwater constituents that may affect neutralization of high pH soil and groundwater.

1.2.1 Hydrogeologic Conditions

A brief description of the HCIM Area and Shoreline Area is provided in this section. A more thorough description of these areas is provided in the CMS Work Plan.

1.2.1.1 HCIM Area

The barrier wall was installed in 2003 and is used to contain contaminated soil and groundwater within the HCIM Area, where most of the site manufacturing and production occurred. The HCIM barrier wall

is keyed into the Upper Aquitard, as discussed in Section 2 of the CMS Work Plan. The HCIM Area is shown on Figure 1. Since late February 2004, the mean groundwater level inside the barrier wall, as measured in MW-49, has been more than 1 foot below the mean groundwater level measured in the downgradient control well outside of the barrier wall, DM-8, located in the Shoreline Area. These measurements indicate that a constant, inward mean hydraulic gradient has been achieved and maintained for the HCIM Area. Groundwater is pumped from the HCIM Area at a rate of about 4 gallons per minute. The barrier wall and groundwater recovery system have effectively isolated groundwater within the HCIM Area from groundwater outside the barrier wall and beneath the aquitard underlying the HCIM Area. The surface cover for the HCIM Area limits infiltration of surface water. Most of the groundwater recovered from the HCIM Area is expected to flow upward, through the aquitard. For more discussion on the hydrogeologic conditions of the HCIM Area, see Section 2 of the CMS Work Plan.

1.2.1.2 Shoreline Area

The Shoreline Area consists of the strip of land west of the HCIM Area along the Duwamish Waterway and south of the HCIM Area along Slip 6. The Slip 6 portion of the Shoreline Area extends to the Boeing property line along the north side of Slip 6. Groundwater flow in the Shoreline Area is essentially stagnant. The presence of the barrier wall along nearly the entire Shoreline Area means that groundwater cannot flow freely from the HCIM Area toward the adjacent surface water, as occurred prior to construction of the barrier wall. Therefore, tidal changes from the Duwamish Waterway and Slip 6 move the nearly stagnant water within the Shoreline Area up and down along this strip of land, and surface infiltration from unpaved portions of the Shoreline Area infiltrate and drain to surface water within shallow Shoreline Area soils. The presence of the barrier wall near the eastern end of the Slip 6 Shoreline Area results in groundwater entering Slip 6 near the southeast corner of the barrier wall. Additional discussion of groundwater conditions in the Shoreline Area is presented in Section 2 of the CMS Work Plan.

1.2.2 Groundwater Chemistry Data

Groundwater data have been collected at the site as part of several investigations and monitoring events since the mid-1990s. As noted above, pH data for groundwater collected since 2008 were used to delineate the high pH area (Figures 1 and 2); the more recent pH data were used to reflect current groundwater conditions (Table 1). These data were taken from quarterly monitoring reports and routine monitoring since January 2008, the Shoreline Soil and Groundwater Characterization Data Report (AMEC, 2012), and non-routine sampling conducted in 2014, as indicated on Table 1.



Table 2 summarizes the data for pH, total alkalinity, and total silicon for existing wells located within the pilot study area and for wells MW-43 and MW-44, which represent monitoring wells with the highest historically observed pH values. The pH data in Table 2 were collected from 2008 to present. The total alkalinity and silicon data for MW-29, MW-53, and MW-54 were collected in 2014. MW-29 data in Table 2 also includes silicon and alkalinity data from the 2005 quarterly monitoring data. For the wells outside the barrier wall (MW-43 and MW-44), the total alkalinity and total silicon data in Table 2 are from the 2005 quarterly monitoring data. The Table 2 data reflect the range expected for these key chemistry parameters for groundwater within the high pH target area. Table 3 summarizes overall water chemistry data for site groundwater. The Table 3 data were taken from Round 28 monitoring data in June 2005; this monitoring event occurred after Shoreline Area groundwater had adapted to conditions after barrier wall construction and during the period of detailed groundwater chemistry monitoring, as discussed in Section 2.0.

2.0 CHEMICAL EQUILIBRIUM MODELING

To support conceptual design of the neutralization system for the pilot study area, chemical equilibrium modeling was used to analyze groundwater chemistry in high pH areas, and the model results were compared to data collected within the high pH target area wells. The chemical model using Visual MINTEQ was developed by using detailed water chemistry results for MW-44, one of the wells in the target area with the highest detected pH readings outside the HCIM area. The water chemistry data were used to assess groundwater chemistry throughout the target area and to simulate changes in water chemistry caused by CO₂ injection. The purpose of the modeling was to estimate how much carbonic acid would be required to neutralize groundwater within the high pH target area, the resulting changes in chemical equilibria caused by adding an acid into site groundwater, and the magnitude of solids precipitation caused by acid addition. These factors were used to support the design of the pilot study inside the barrier wall. The high silicon concentrations in high pH groundwater are expected to cause precipitation of silica as the pH is reduced. The precipitated solids could affect aquifer characteristics and cause fouling, which may affect follow-up injections in a fixed injection well.

The chemical equilibrium model was used to assess copper solubility based on water composition in the monitoring wells in the southwest corner of the site where the copper plume is present (Figure 3-21 of the CMS Work Plan). Results from the equilibrium model were compared to the dissolved copper concentrations measured in groundwater samples from these wells. The model predictions for dissolved copper were significantly lower than observed. Based on model predictions, more data, such as the presence of ligands and redox conditions, would be required to characterize the groundwater chemistry that may be affecting copper solubility. As a result, copper solubility during pilot study injections will be evaluated using field samples, as described in Section 4.4. A copper solubility curve may be generated from the groundwater data collected during CO₂ injections to assess the potential for copper mobilization or reduction as a result of CO₂ neutralization.

2.1 METHODS

Detailed groundwater chemistry was monitored in the Shoreline Area after barrier wall completion to determine the effect of the barrier wall on the groundwater chemistry; the detailed groundwater chemistry data were collected from the third quarter of 2003 to the fourth quarter of 2005. Figure 3 shows the trends for pH and total dissolved silicon in MW-44 over this monitoring period. As shown on Figure 3, the pH and silicon trends appear to be leveling out and approaching a new state of equilibrium between the soil and stagnant groundwater after barrier wall construction in 2003. Chemical equilibrium modeling was performed using the groundwater composition for the second quarter of 2005 in well MW-44, as it has historically been one of the highest pH wells. Data from the



second quarter of 2005 were used as the pH appeared to be leveling out at this point, and the dissolved silicon concentration was slightly higher than the average observed in this well in 2005. The water chemistry data for MW-44 that were used for modeling are summarized in Table 3. Table 3 also shows groundwater data for the other wells sampled for the Round 28 monitoring report.

Visual MINTEQ was used to model the aqueous equilibria for neutralizing groundwater based on the MW-44 composition from 2005. The initial constituent concentrations from the laboratory analyses were input into the model to establish the initial equilibrium speciation. In order to model alterations to the water chemistry due to injection of CO₂, the modeled system was assumed to be in equilibrium with ferrous hydroxide, amorphous silica, and gaseous CO₂. For initial conditions, the gaseous CO₂ partial pressure was established for equilibrium with the measured alkalinity. Injection of CO₂ was simulated by increasing the partial pressure of CO₂ in a series of steps and recalculating aqueous equilibria. The increased CO₂ partial pressure increased the amount of carbonic acid that dissolved into the system, simulating what would happen if CO₂ was injected to the subsurface, creating increasing partial pressure of CO₂. For each incremental increase in CO₂ partial pressure, the aqueous chemical system was speciated using Visual MINTEQ to simulate the resulting pH, dissolved silica, and total dissolved iron. Precipitation was determined by the change in total species concentration of silicon and iron for each CO₂ partial pressure increment. Precipitated solids were assumed to be amorphous silica (SiO₂) and ferrous hydroxide. Precipitation of other constituents was considered to be insignificant due to low initial concentrations, and was not accounted for in the modeling.

2.2 GROUNDWATER CHEMISTRY MODELING RESULTS

The results for total SiO₂ vs pH from the equilibrium modeling are shown on Figure 4 as a dashed red line. Figure 4 also shows pH versus measured total SiO₂ for wells MW-41, MW-43, and MW-44 from the third quarter of 2003 to the fourth quarter of 2005, with pH ranging from 9.3 to just over 11. As shown, the model predictions for the equilibrium dissolved silica concentration compare well with the sample analyses for these wells up to a pH of about 10.8. New data collected in 2014 for MW-53 are also shown on Figure 4 and indicate agreement between the model predictions and the analytical results. This agreement indicates that the assumptions used to develop the chemical equilibrium model, including using the water composition data for MW-44, are applicable to actual Shoreline Area groundwater conditions at the site. The model output, using water composition data from one data set for MW-44, reproduced with reasonable accuracy the measured concentrations of silica in wells MW-41, MW-43, MW-44, and MW-53, indicating that high pH groundwater at the site is saturated with amorphous silica.

The model results indicate that approximately 1,300 milligrams per liter (mg/L) of solids, primarily consisting of amorphous silica, will precipitate from the addition of CO₂ to bring the pH down to 8.5 standard units (SU). Figure 5 shows the total amount of dissolved CO₂ needed to lower the pH from an initial value of 10.8 to 6.5 Standard Units (SU) (approximately the site background pH) and the required partial pressure of CO₂ to deliver the dissolved mass of CO₂ into groundwater, based on MW-44 groundwater data. As shown on Figure 5, the model predicts that a total of 3,500 mg/L of CO₂ must be dissolved into the groundwater, requiring a partial pressure of 1.1 atmospheres of CO₂ to reduce the pH of the water from 10.8 to 6.5 SU. The CO₂ dose to neutralize groundwater with lower initial pH values can be estimated from the difference between starting and ending pH values.

While the model may be used to gain an understanding of how groundwater will behave during neutralization; several limitations should be noted. First and foremost, the model does not address the soil buffering capacity for the soils assumed to be in equilibrium with the groundwater at the present time. Aqueous equilibria and precipitation reactions will proceed relatively rapidly, but reactions with the soil will proceed more slowly due to surface and pore diffusion and dissolution. It is expected that the soil buffering capacity will slowly cause the groundwater pH to increase after the initial rapid neutralization of the groundwater. It is expected that amorphous silica will precipitate onto soil particles as a result of groundwater neutralization. The increase in pH from soil reactions is expected to cause partial dissolution of amorphous silica back into the water column as the pH rebounds.



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3.0 PILOT STUDY OBJECTIVES

The purpose of the pilot study is to assess the effectiveness and practicality of CO₂ injection for neutralizing high pH groundwater to support evaluation of this technology in the CMS. The CO₂ neutralization pilot study will evaluate the technical feasibility of CO₂ injection to neutralize the high pH in the target area, assess injection costs, and evaluate factors affecting injection system design. The general pilot study objectives, which were adopted in part from a previous CO₂ injection study (Mutch, 2013), are:

1. Estimate the amount of CO₂ that would be consumed to neutralize high pH groundwater and soil in contact with the high pH groundwater.
2. Assess CO₂ practical injection rates within the site.
3. Estimate the practical radius of influence (ROI) for CO₂ injection wells.
4. Evaluate the effect on the formation and collapse of groundwater mounding caused by injection of gaseous CO₂.
5. Evaluate the kinetics of high pH groundwater neutralization and pH rebound.
6. Evaluate the CO₂ utilization efficiency and CO₂ consumption required to neutralize high pH groundwater and soil in the field.
7. Evaluate potential changes in aquifer characteristics that may result from CO₂ injection.
8. Evaluate changes in geochemistry and other parameters that may result from CO₂ injection.

The above pilot study objectives and data quality objectives (DQOs) are described in more detail in Table 4 and discussed in Sections 3.1 to 3.8. These objectives and DQOs support evaluation of the potential effectiveness of CO₂ injection in achieving neutralization objectives and provide information needed for the conceptual design and cost estimates required to evaluate this remediation approach for neutralization of groundwater within the Shoreline Area in the CMS. A conceptual level design is necessary as part of the CMS for evaluation and selection of the preferred remedy for the former Rhone-Poulenc site; the pilot study objectives and DQOs are sufficient to support the conceptual level design needed for the CMS. The pilot study also may provide information that could be used in full-scale design if the technology is determined to be feasible.

Data collection methods and DQOs to be used to support the objectives summarized in Sections 3.1 through 3.8 are described in more detail in Section 4 and Table 4.

3.1 INITIAL CO₂ CONSUMPTION ASSESSMENT

The pilot study will determine the CO₂ demand to neutralize a unit volume of both soil and water in the target area. Prior to CO₂ injection, the high pH groundwater will be in equilibrium with the soil matrix. The chemistry of the soil surfaces, including internal pore surfaces, likely has been affected by the high pH groundwater, which has been in contact with these soils for decades. It is anticipated that as CO₂ is injected and dissolves into the groundwater as carbonic acid, the carbonic acid will neutralize groundwater alkalinity, decreasing the groundwater pH and causing amorphous silica to precipitate onto the surfaces of subsurface soil. As the pH in the groundwater declines, a concentration gradient will form between the soil surfaces and the groundwater, resulting in diffusion of acid from the groundwater to the soil surface, where it will react with alkaline compounds on the soil. It is expected that initially, the acid buffering capacity of the soil will be greater than the acidity injected into groundwater. As the injected acid is consumed by the soil buffering capacity, it is expected that a rebound in the groundwater pH will be observed. The pH rebound is expected to be slow relative to aqueous equilibria and mineral precipitation reactions due to the kinetics of diffusion and dissolution processes. It is expected that several neutralization cycles will be required to fully neutralize the high pH-affected soil.

The total dose of CO₂ needed to achieve full neutralization will depend on the groundwater alkalinity and the soil buffering capacity. To achieve remediation of the high pH area, both soil and groundwater will need to be neutralized. The carbonic acid demand for groundwater may be readily and accurately determined from the measured groundwater alkalinity and concentrations of other constituents determined from sample analyses and using a model such as Visual MINTEQ, as described in Section 2. The soil buffering capacity is more complex and must be empirically evaluated to determine the total acid dose required to fully neutralize subsurface soils to achieve a defined groundwater pH. To accurately assess the soil buffering capacity, soil samples representative of the predominant soil types within the high pH plume must be collected and tested in the laboratory. Methods to evaluate the soil buffering capacity are outlined in Section 4.3. Together, the groundwater alkalinity, buffering capacities of representative soils, and quantities of the different soils within the high pH plume will determine the total amount of CO₂ required for neutralization. It is expected that the greatest uncertainty for this determination will be in the estimated quantities and compositions of the affected soils (e.g., silts will be more difficult to neutralize than sands).

3.2 CO₂ INJECTION RATES AND INJECTION PRESSURES

The relationship between injection pressure and injection rate is site-specific and needs to be evaluated in the field. An optimal operating point for CO₂ injection needs to be identified to evaluate the feasibility of injecting CO₂ to neutralize the high pH target areas. The injection pressures will

depend on aquifer and well characteristics, requiring site-specific measurements. As silica precipitates during neutralization, the injection pressures required to maintain a given injection rate may increase, and the pilot study should assess the potential for these changes. Details for the plan to assess the pressure/flow rate relationship and data collection is described in Sections 4.4.1 and 4.4.3.

3.3 RADIUS OF INFLUENCE

The ROI for CO₂ injection wells is a site-specific characteristic that must be evaluated in the field to determine the number of wells needed to effectively remediate the target area without adversely affecting areas with acceptable pH levels and to avoid loss of CO₂ to adjacent surface water bodies. The ROI is affected by injection rate and lithology, and should be measured for different gas injection flow rates. As the CO₂ injection flow rate is increased, the ROI is expected to increase, within limits. However, excessively high injection rates may create gas channels that would decrease the effective ROI, even though neutralization may be observed at greater distances from the gas injection location due to the formation of gas channels. The ROI evaluation only needs to provide a general understanding of the area addressed by injection in a single well; it is not necessary to accurately characterize the ROI, as it may vary with well location due to soil heterogeneity. The ROI will be used to determine the number of wells needed to neutralize the target area; the ROI for individual wells can be changed during operation by changing the injection flow rate. Additionally, if the actual ROIs in a full-scale system differ from that determined in the pilot study, injection wells can be added to fully address the target area without substantially increasing remediation costs. Details for assessing the ROI are presented in Sections 4.4.1 and 4.4.3.

3.4 GROUNDWATER MOUNDING

Groundwater mounding occurs during gas injection through the temporary displacement of groundwater in soil matrix pore spaces. The groundwater mound forms as the gas displaces the groundwater upward and laterally in the vicinity of the injection area. Once the gas has moved to the groundwater surface, the mound dissipates radially outward. When gas flow ceases, the gas-filled pores become re-saturated with groundwater and the mound collapses, resulting in a temporarily depressed groundwater table (USACE, 2013). Cycles of groundwater mound formation and collapse create mixing conditions in the injection zone. Groundwater mounding will be assessed by measuring groundwater elevations within the injection area, as described in Section 4.4.1. Only a general understanding of groundwater mounding and collapse characteristics is needed, as this is an operational parameter that can be controlled during injection operations. A general understanding will be sufficient to assess this technology in the CMS and to estimate operations and maintenance costs.

3.5 ASSESSMENT OF PH NEUTRALIZATION AND REBOUND RATES

The rate at which groundwater is neutralized will be evaluated during the pilot study. The rate of neutralization will need to be balanced with the utilization efficiency of the CO₂ injected and the ROI to determine an optimal injection flow rate. The neutralization rate of the groundwater is expected to be a function of the CO₂ injection flow rate. The rate of neutralization will be assessed using pH loggers placed in observation wells, as described in Section 4.4.1 through 4.4.4. The neutralization rate requires only general characterization, as it will be affected by variation in groundwater chemistry and soil types; a full-scale system would include pH monitoring to assess actual neutralization rates and to control operations.

As discussed in Section 3.1, pH rebound will likely occur after the pH of the groundwater has been reduced and CO₂ injection is stopped. Groundwater pH is expected to increase as the soil buffering capacity reacts slowly with the groundwater. The time scale for pH rebound must be assessed in the pilot study to estimate the time required for neutralizing the target zone. The rate of rebound will likely change after multiple injections and is likely dependent on several factors, such as natural variation in soil type, precipitation of amorphous silica, and groundwater pH. To gain a better understanding of pH rebound, groundwater pH will be monitored within the neutralized area after CO₂ injection is stopped. The rate of pH rebound needs to be assessed in addition to any permanent pH decrease achieved by CO₂ injection. The pH rebound characteristics need only be generally characterized, as actual characteristics will likely depend upon the actual soil type distribution in the target areas outside the HCIM area. The plan for assessing pH rebound, including data collection requirements, is presented in Section 4.4.4.

3.6 CO₂ UTILIZATION EFFICIENCY AND CONSUMPTION

The utilization efficiency for CO₂ is the percentage of injected CO₂ that dissolves into groundwater and is available for neutralizing the groundwater and soil. It is expected that only a portion of injected CO₂ will dissolve into the groundwater; undissolved CO₂ will migrate to the surface and be released to the atmosphere. CO₂ utilization efficiency is important in determining the cost of injecting gaseous CO₂ into the subsurface for neutralization. It is expected that the utilization efficiency will be affected by the injection rate. As the CO₂ is injected, the gas will follow preferential flow paths, such as high permeability soils, natural or constructed surface vents, or debris in the ground, that may provide a conduit or barrier for the gas. High injection rates would likely cause channels of gas to form from the injection point to the vadose zone. It is expected that CO₂ gas bubbles will be present within the injection zone. These gas bubbles are expected to either slowly dissolve as CO₂ is utilized to neutralize soils, or they may coalesce and could move upward, toward the surface.

In order to assess the efficiency of utilization for CO₂, changes in groundwater total carbonate/CO₂ must be monitored before and after injections to estimate dissolution of injected CO₂. The CO₂ utilization efficiency will be assessed as described in Section 4.4.1 and 4.4.2.

3.7 CHANGES IN AQUIFER CHARACTERISTICS

The potential for changes in aquifer characteristics will be evaluated as part of the field testing program described in Section 4.4. It is anticipated that as the groundwater is neutralized, amorphous silica (and possibly other silicates) will precipitate onto the subsurface aquifer soil matrix. This precipitation may impact the effective soil porosity and could result in reduced aquifer permeability. This effect will be addressed as described in Section 4.1. Changes in aquifer characteristics will likely be variable and depend on factors such as initial pH, soil type, and overall groundwater quality. The effect may also be temporary. Due to the potential for variation, only a general understanding is needed to assess CO₂ neutralization as a potential remedy for the site. If substantial changes are noted in aquifer characteristics in the pilot study, the full-scale design can be adapted to address the changes.

3.8 CHANGES IN GROUNDWATER AND SOIL CHEMISTRY

Characterization of the soil and groundwater chemistry changes resulting from injection of CO₂ will provide insight into the groundwater/soil systems' response to changes in pH that may affect ongoing injection operations and attainment of neutralization objectives. The pilot study will include groundwater sampling and analysis before and after groundwater neutralization during bench testing and before and after field injections to assess water chemistry changes caused by CO₂ injection. The analyses will identify changes in groundwater concentrations for the analytes discussed in Section 4.0. The groundwater analyses will be used to support and assess equilibrium modeling for system analysis. The results from the pilot study are expected to be confirmed by equilibrium modeling, allowing the equilibrium model to be used in the future to accurately predict the effect of neutralization on groundwater chemistry and the potential for precipitation of dissolved components.



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4.0 PILOT STUDY METHODS

Pilot testing will be conducted to assess injection of CO₂ into areas affected with high pH to reduce the pH. The pilot study methods described in this section have been developed to achieve the objectives and DQOs described in Section 3 and Table 4 of this work plan. Each component of the pilot study is summarized in Table 4 and related to the DQOs discussed in Section 3.0. The field component of the pilot study will be performed in four phases, as described in Table 4 and in Section 4.4.

Pilot testing will be conducted inside the barrier wall to reduce the potential for adverse impacts to adjacent surface water that could occur during injections in the Shoreline Area. This location will support evaluation of a wider range of conditions than could be safely evaluated in the Shoreline Area. Groundwater chemistry and soil composition within the high pH areas inside the barrier wall appear to be similar to conditions within the Shoreline Area, outside the barrier wall, as can be seen by comparing the data point for MW-53 (inside the barrier wall) to the pH results for MW-41, MW-43, and MW-44 (outside the barrier wall) (Table 2 and Figure 4).

The area near well cluster MW-43/MW-44 in the Shoreline Area contains some of the highest pH levels observed historically at the site (Figure 1). Pilot field testing will be conducted using a new gas injection well located approximately 7 feet north-northwest of MW-53 and 10 feet northwest of MW-54; this new injection well will be located directly across the barrier wall from wells MW-43/MW-44 and the high pH target area (Figure 6). The injection well will also be located near the barrier wall, which will allow effects of the barrier wall on CO₂ injection to be evaluated; this location is similar to and mirrors the likely injection locations within the high pH target area located outside the barrier wall. The high pH target area located outside the wall is also substantially covered with an asphalt cover, although a portion of the Shoreline Area (located immediately along the shoreline) has vegetative cover (Figure 1).

Table 2 shows pH, total alkalinity, and total silicon analytical data for wells MW-43/MW-44 and for wells MW-53/MW-54 and MW-29, which will be included in the pilot study injection monitoring well network. The parameters shown on Table 2 are some of the key water chemistry parameters affecting neutralization. Well MW-53, which is about 8 feet away from MW-54, is completed in the shallow portion of the Upper Aquifer, and had a pH of 10.79, as measured in the laboratory during alkalinity testing of a sample collected in the first quarter of 2014. This pH is slightly lower than the pH observed in wells MW-43/MW-44 in the first quarter of 2014. The pH in MW-54, completed in the deep portion of the Upper Aquifer, had a pH of 10.52 during field measurements in June 2014. The total alkalinity in wells MW-53/MW-54 is lower than observed in wells MW-43/MW-44. Results for total silicon in wells



MW-53/MW-54 are generally consistent with results for wells MW-43/MW-44, although the single silicon measurement for MW-54 was significantly higher than for wells MW-43/MW-44 and the alkalinity was lower in MW-53/MW-54. Sampling for water chemistry in MW-53/MW-54 has been limited, but wells MW-43/MW-44 were regularly sampled for water chemistry during 2004–2005. The new injection well will be located about 44 feet from wells MW-43/MW-44 and near the edge of the high pH target area, which will assist in evaluating effects of injection on areas with lower pH levels, as will be encountered when approaching the edges of the high pH target area outside the barrier wall. Well MW-29 is approximately 31 feet from the new injection well and is screened in the shallow zone of the aquifer.

Bench testing will be conducted as part of the pilot study to assess the total amount of acid required to neutralize the soil and the groundwater, the potential for solids precipitation, and changes in groundwater geochemistry caused by neutralization. CO₂ injection testing will be conducted as part of the field study to evaluate the injection pressure and flow rate relationships that can be safely delivered to the subsurface. The injection testing will also be used to characterize the ROI achieved by the different injection flow rates and to identify the characteristics of the formation and collapse of groundwater mounding. The ROI will be evaluated by monitoring pressure, groundwater levels, groundwater pH, and total inorganic carbon (TIC) in several observation wells. Pressure readings will identify increased pressure created by CO₂ injection. Groundwater level measurements in the observation wells will identify mounding created by CO₂ injection. The TIC measurements will identify how much CO₂ has been dissolved into the groundwater. The ROI evaluation will be based on the measured increase in pressure, water levels, and TIC; the decreased pH measured in the observation wells will also be used to support evaluation of ROI. The rate at which groundwater is neutralized and the rebound of the groundwater pH after CO₂ injection is stopped also will be evaluated by monitoring pH in the pilot study observation wells. Groundwater samples will be collected from injection and observation wells to document changes in groundwater chemistry prior to, during, and after CO₂ injections and during the expected pH rebound period. A summary of sampling and analyses for all components of the pilot study is provided in Table 5 and discussed in the relevant sections below.

Pilot field testing also will be directed toward assessing the effect of the injection rate on the utilization efficiency of the CO₂. In order for CO₂ to neutralize the high pH, the CO₂ must dissolve into the water; a high surface area between the gaseous CO₂ and groundwater will increase mass transfer efficiency. It is expected that high CO₂ injection rates will cause gas channels to form in the saturated zone that would decrease the gas surface area, resulting in decreased dissolution rate for the gas and increased gas flow to the vadose zone and ultimately to the atmosphere. As noted in the U.S. Army Corps of Engineers (USACE) Engineer Manual *In-Situ Air Sparging* (USACE, 2013), optimal mass transfer is anticipated to occur at intermediate injection rates, when an appropriate distribution of flow

channels forms. The USACE manual indicates that optimal flow occurs when injecting gas at the highest pressure that does not cause fracturing of the formation. Vented CO₂ may be monitored in one vent well completed in the vadose zone, and changes in water chemistry will be monitored in the pilot study observation wells and the vent well screened partially beneath the water table to estimate changes in total carbonate species (as indicated by an increase in TIC). There also is potential for injected CO₂ to migrate outside the observation area due to unknown preferential flow paths or via channels created from excessively high injection pressure. Any gas migration beyond the observation area may not be detected. A mass balance on total CO₂ injected and the CO₂ dissolved into the groundwater target areas will be performed to evaluate CO₂ utilization efficiency; this mass balance may be approximate due to the potential for unknown or unexpected flow paths. The mass balance will be based on the quantity of CO₂ injected and the measured increase in TIC within groundwater.

Aquifer slug testing will be performed in the new injection well and selected pilot study observation wells to evaluate potential changes in aquifer permeability as a result of neutralizing the groundwater in the vicinity of the CO₂ injection well. Slug testing will be performed prior to any injections to establish a baseline and after injections have been completed. Groundwater sampling will be conducted before commencing CO₂ injection to establish baseline conditions and after stopping CO₂ injection to assess changes caused by the injection of CO₂. Details for the pilot study field work are discussed below. Monitoring associated with the groundwater bench testing is discussed in Section 4.3.1 and the field testing is discussed in Section 4.4 and summarized in Table 5.

4.1 AQUIFER SLUG TESTING

This section describes the aquifer slug testing procedures that will be implemented for selected pilot study wells to assess potential changes in aquifer permeability characteristics due to CO₂ injection. Testing will be performed following the construction and development of the new injection and observation wells. Slug testing will be performed to measure the average hydraulic conductivity of the formation surrounding the new injection well, existing monitoring wells MW-53 and MW-54, and well IMW-A1-D. These wells are located nearest to the center of the CO₂ injection area and are expected to be most highly affected by CO₂ injection.

The new injection well will be installed, developed, and surveyed for location and elevation. Prior to slug testing, the initial depth to water will be measured and recorded from the top of the well casing in each of the three slug test wells. An unvented pressure transducer/logger will be placed within each well to record water levels during slug testing. The length of the cord used to suspend the transducer/logger will be carefully measured prior to installation, and the initial depth-to-water measurement will be used to check the accuracy of the transducer/logger readings. A BaroTROLL or equivalent barometric measurement instrument will be used to record barometric pressure to



compensate the well transducer readings for atmospheric pressure. The pressure transducers/loggers will be placed into each well and lowered to just above the bottom of the well. The pressure transducer/loggers will be set to record data at short intervals (e.g., every second) for the aquifer slug testing.

Each slug test will consist of a falling-head phase and a rising-head phase. During the falling-head (or slug-in) phase, a 1.5-inch-diameter, 4-foot-long, solid polyvinyl chloride (PVC) rod or slug (filled with sand and sealed) will be quickly lowered into the well with a rope affixed to the top of the slug by hand so that it is completely submerged. Care will be taken during slug insertion to minimize disturbance of the transducer/logger or the transducer/logger cable. The water level rise resulting from displacing water in the well will be monitored both by the transducer/logger and by manual water level measurements. After the water level becomes stable (defined as less than a 0.1-foot change in readings within 10 minutes), the slug will be quickly removed from the well by hand to initiate the rising-head (or slug-out) phase. This phase will be complete when the water level returns to its initial, pre-test, level and becomes stable using the same criteria as for the falling head phase. In addition to transducer data, field personnel will record depth-to-water measurements and time until the water level in the well approaches the level at which it was recorded prior to the start of the slug test. After the slug-out test is complete at the well being tested, the pressure transducer/logger will be removed, and the well casing will be prepared for the pilot field study, as discussed in Section 4.2.

The recorded water level data will be analyzed using AQTESOLV software (or equivalent computational methods) to estimate the hydraulic conductivity of the aquifer materials near the screens of the seven wells that were tested. Similar slug tests will be completed in these same wells after completion of the pilot study to assess potential impacts to aquifer permeability induced by CO₂ injection.

4.2 CO₂ INJECTION, OBSERVATION, AND VENT WELL DETAILS

To conduct the pilot study, several new observation wells and a new vent well will be installed to collect data in support of the pilot study objectives. A new injection well will also be installed to inject CO₂ for the pilot study. Existing monitoring wells MW-53/MW-54 and MW-29 will be used in conjunction with the new observation wells to collect pilot study data. One new vent well will be installed to vent any CO₂ that migrates to the surface in the vicinity of the injection well during the pilot study. The layout of the pilot study wells is shown on Figure 6.

Figure 7 presents a cross section across the pilot study area perpendicular to the barrier wall depicting the lithology based on boring logs for nearby wells. Figure 7 also shows the new and existing pilot study well screen depths and screen intervals across the pilot study area perpendicular

to the barrier wall. Approximate depths and spacing of each pilot study well are summarized in Table 6. Drawing 1 shows well construction details for the new injection, vent, and observation wells to be installed for the pilot study. The new wells will be installed using direct-push or hollow-stem auger drilling methods. The injection and observation wells will be developed after installation. All new wells will be surveyed for location and top-of-casing elevation. The injection well will be installed first to collect bench testing soil samples and to confirm subsurface conditions. The observation and vent wells will be installed after the injection well.

The pilot study area, which includes the CO₂ injection well, vent well, and observation wells, will be enclosed within temporary fencing to protect equipment and personnel during pilot study injection and monitoring activities. The temporary fencing will be locked, and signage will warn of pressurized gas lines. The approximate layout for the temporary fencing is shown on Figure 6.

4.2.1 CO₂ Injection Well

CO₂ will be injected into the new injection well (Figure 6) during testing. The new injection well will be screened at a depth and within soil types similar to those for well MW-43, which is located outside the barrier wall and within the high pH target area to be remediated (Figure 7). The depth of the 5-foot injection well screen was selected to target the silty sand within the “Lower Aquifer Unit”; the bottom of the screen will be placed at the top of the silt aquitard that defines the base of the area within the barrier wall. The injection well construction details are provided on Drawing 1 and Table 6. The injection well screen depth and length may be adjusted from the approximate values shown in Drawing 1 and Table 6 depending on the soil types and groundwater pH values encountered in the field during well installation. The top of the sand pack for the injection well will be a minimum of 6 inches below the top of the silty sand unit.

Soil samples for bench testing will be collected from the injection well boring. If the soil pH conditions encountered at the target depth for the injection well are lower than expected during injection well installation (i.e., lower than about 10.5 SU), the injection well location may be changed. If the injection well location is changed, the pilot study well layout presented in Figure 6 will be maintained to the extent practicable; however, the distance to existing wells MW-29, MW-53, and MW-54 will change. If injection well relocation would likely make the existing wells unusable for the pilot study, the U.S. Environmental Protection Agency (EPA) will be notified prior to injection well installation.

Drawing P&ID 01 shows the planned configuration of the CO₂ injection system. Pilot study equipment requiring electricity may be located near the existing groundwater pretreatment building or, potentially, adjacent to the pilot study area (as shown on Figure 6), depending on cost and availability of electricity and space constraints. The liquefied CO₂ storage tank(s), pressure relief valves, solenoid



valve and timer, heater, flow controller, pressure regulator, and the CO₂ injection flow meter (CO₂ gas system) may be located adjacent to the existing groundwater pretreatment building along the north side of the property or adjacent to the pilot study area. If the CO₂ gas system is located adjacent to the existing groundwater treatment plant, pressure tubing to transfer CO₂ from the CO₂ gas system to the injection well will be run along existing perimeter fencing.

Aboveground pressurized piping for the CO₂ injection system will be high-density polyethylene (HDPE) and/or galvanized steel. A manual shutoff valve and a pressure relief valve also will be located at the wellhead for the injection well, as shown on Drawing P&ID 01. The wellhead for the injection well will be constructed to allow the well to be pressurized with CO₂ for injection. A Schedule 80 PVC adapter will be glued to the Schedule 80 well casing to accept threaded HDPE or galvanized steel fittings. The fittings will support installation of tubing/piping, a pressure indicator, a pressure relief valve, and a shutoff valve, as shown on Drawing P&ID 01. Teflon tape will be used to seal all threaded joints. Gas-tight compression fittings will be used to run any tubing or instrument cables into the wells. All materials selected for the injection system will be confirmed to be compatible with CO₂ and will be able to safely contain expected pressure and flow ranges.

4.2.2 Observation Wells

Existing groundwater monitoring wells MW-29 (approximately 31 feet away from the injection well) and MW-53/MW-54 (approximately 7–10 feet away from the injection well) will be used as observation wells during the pilot study. In addition, seven new observation wells, or injection monitoring wells (IMWs) will be installed at varying distances and depths to monitor the ROI, CO₂ utilization efficiency, groundwater mounding, and changes in groundwater chemistry (Table 6 and Figures 6 and 7). All of the observation wells will be used to collect data for the pilot study which will include well casing pressure. Groundwater samples will also be collected from the observation wells during the pilot study. Monitoring and sampling details are discussed in Section 4.4.

Drawing 1 shows the construction details for the new observation wells, and Drawing P&ID 01 shows the piping and instrumentation details for the new and existing observation wells for the pilot study. Table 6 summarizes the approximate depths of the observation well screens relative to the injection well, and the approximate spacing between the observation wells and the injection well. The new observation wells will be installed with 2-inch schedule 80 PVC screened over a 10-foot interval, except for the deeper (“D”) observation wells at points “A1,” “B1,” and “B2” (Figures 6 and 7), which will be screened across the silty sand unit expected to be encountered during field installation. The observation wells will be completed with flush, heavy duty surface monuments.

The existing observation wells (MW-53/MW-54 and MW-29) will be modified by installing a schedule 80 PVC adapter that will be glued to the existing Schedule 80 well casing to accept threaded schedule 80 PVC fittings. As shown on Drawing P&ID 01, a schedule 80 PVC ‘Y’ or ‘Tee’ fitting will be installed to allow for a pressure indicator and pressure transducer/logger to be installed for each observation well. The observation wells utilizing data loggers also will be equipped with a submersible transducer/logger and a submersible pH and temperature probe/logger. Recorded water levels, pH readings, and temperatures will be downloaded by removal of the loggers from the wells (or downloaded from the wellhead if practicable). The top of the casing for the new observation wells will be threaded so that a threaded pipe cap can be installed to make a gas-tight seal. The pipe cap will be tapped to install a hand valve and pressure gauges and/or pressure logging transducers.

4.2.3 Vent Well

The pilot study design includes one new vent well that may be used to vent any CO₂ passing through the vadose zone. During active injection events, the vent well may be sampled to monitor the CO₂ concentration in the vent gas using a portable CO₂ meter.

Drawing 1 shows the construction details for the new vent well, and Drawing P&ID 01 shows the planned instrumentation for the vent well. Figures 6 and 7 show the location and layout of the vent well in relation to the injection and observation wells. Table 6 summarizes the approximate depths of the vent well screen relative to the injection well and the approximate spacing between the wells. The new vent well will have a 15-foot screen length that will be placed so that it extends partially into the top 10-feet of the groundwater table. The vent well will also include a logging pH and temperature probe, which will provide pH and temperature data at the top of the saturated zone near the injection well. The bottom of the well screen in the new vent well will be installed 10-feet below the groundwater level encountered during installation. The new vent well will be constructed with a 2-inch schedule 40 PVC casing. The top of the vent well will be mounted flush to the existing pavement surface, similar to existing groundwater monitoring wells. A threaded cap will be installed on the vent well casing. The cap will be drilled and threaded to accept a pressure gauge and/or pressure logging transducer, and shutoff valve.

4.2.4 Well Construction Details

All new wells will be drilled by a driller licensed in the State of Washington. Observation wells will be installed using direct push technology, and the new injection well will be installed using a hollow-stem auger rig under the supervision of a Washington State licensed geologist. Prior to drilling, a private utility locator will be hired to locate subsurface utilities in the area of the proposed drilling locations. Qualified Amec Foster Wheeler staff will work with the site engineers to identify known underground



utilities in the area. Sample and well locations will be adjusted in the field to avoid any underground utilities identified and may be adjusted based on lithology encountered during installation. Well screen lengths may be adjusted in the field based on lithology encountered to ensure that the target lithologic units are screened.

The injection well hollow stem auger boring will be continuously logged to a depth ending at the silt layer for lithology and for collection of soil samples for bench testing. The observation well borings will be backfilled to the target well depth using medium bentonite chips. The injection well boring will be backfilled with bentonite grout slurry. Drill cuttings from the well installations will be placed directly into drums and labeled with the contents and date. The drill cuttings will be sampled for proper waste characterization and disposed of in accordance with federal and state laws and regulations. The new wells will be installed using the designs presented in Drawing 1. A heavy-duty flush surface monument will be cemented in place for each new well; the lids will be removed to allow installation of the surface piping needed to conduct the pilot testing. After pilot testing is completed, the surface piping will be removed, and the surface monuments will be sealed to protect the wells. The new wells will be surveyed for location and elevation. The observation and injection wells will be developed prior to use in the pilot study; recovered groundwater will be treated in the groundwater pretreatment plant prior to discharge to the Seattle sanitary sewer system.

As noted in the draft CMS Work Plan, it appears that the caustic soda, which is denser than the groundwater; sank to the lower confining layer just below the silty sand layer, and has been in contact with the lower portion of the aquifer (Figure 2). Based on site characterization data, it appears that the sand (SP) and silty sand (ML-SM) layers within the high pH target area outside the barrier wall have the highest pH values (Figure 7). Based on these observations, soil samples will be collected from these two soil units during installation of the injection well for use in measuring the soil buffering capacity. The soil samples will be collected from the injection well boring noted in Section 4.2.1. The deep boring will be placed in an area of high pH; samples of the SP and the ML-SM soils will be collected using continuous split spoon sampling and tested in the field for pH, starting at approximately 35 feet bgs and extending to the bottom of the boring. The pH of the soils encountered during the injection well boring installation will be checked prior to soil sample collection to verify the soil pH is greater than approximately 10.5. If the soil pH is appreciably lower, the boring will be abandoned in accordance with regulatory requirements and the boring repeated at a new location in order to target soils with high pH levels. Soil pH will be measured by placing a small amount of soil sample in a container and hand mixing with a 1:1 dilution of deionized water. The pH of the resulting solution will be measured with a calibrated, portable pH meter.

4.3 BENCH SCALE STUDIES

Bench scale studies will be conducted to support final design of the pilot study and to characterize the samples collected in the field. Testing will assess neutralization of pH-affected groundwater and soil. The objectives of the bench scale studies are to measure the total acid demand for the groundwater and soil in the target areas, assess changes in groundwater chemistry caused by groundwater neutralization, evaluate temperature effects of neutralization, and verify the chemical equilibrium modeling, as discussed in Section 2.0.

Two different bench scale studies are planned for the CO₂ pilot study. The first involves a groundwater study using high pH groundwater collected from the injection well. The groundwater will be titrated with a mineral acid in a laboratory to neutralize the groundwater, evaluate solids precipitation, and assess the potential for significant exothermic reactions, as discussed in more detail in Section 4.3.1. The second bench study will measure the soil buffering capacity to determine the amount of acid required to neutralize soils from the high pH target area. The soil buffering capacity testing is described in more detail in Section 4.3.2.

4.3.1 Groundwater Chemistry Bench Study

Two groundwater samples will be collected from the new injection well to assess precipitation resulting from neutralization of the high pH groundwater. One groundwater sample will be field filtered and analyzed for total dissolved solids (TDS) and dissolved silica. Another water sample will be collected in a zero headspace container for laboratory testing. During sample collection, field staff will measure the following field parameters: pH, turbidity, conductivity, and temperature. An aliquot will be collected from the water sample container and analyzed for TSS and alkalinity. A second 500-milliliter (mL) aliquot will also be taken from the container to be mixed and titrated with acid down to a pH of 6.5 SU. Water temperature will be measured and recorded during the mineral acid titration to assess the potential for significant exothermic reactions. The sample will be mixed for approximately 24 hours, after which the TSS and dissolved silica of the sample will be measured to determine the amount of solids formed from the addition of the acid.

Results of the titration and sample analysis will be compared to the theoretical modeled dosage of CO₂ required to neutralize groundwater and amorphous silica precipitation (Figure 5), as discussed in Section 2.0. The results will then be used as appropriate to adjust the estimated CO₂ mass loading to meet neutralization objectives during Phase 3 field testing, as discussed in Section 4.4.3.

4.3.2 Soil Buffering Capacity Study

As noted in Section 3.1, in order for target area neutralization to be effective, both groundwater and soil must be neutralized. It is expected that long-term exposure of site soils to high pH groundwater has altered the soil surface chemistry and that the reaction kinetics for soil surface reactions will lead to a slow pH rebound after groundwater is neutralized. The buffering capacity of the soil (the capability of compounds or minerals associated with the soil to react with acid) must be neutralized to achieve the objectives for the high pH target area.

Soil buffering capacity has generally been evaluated in the past to assess using lime to increase the pH of soils in the agricultural industry. One published test method added a base to soil sample aliquots at varying concentrations and allowed the aliquots sufficient time to react before measuring the pH of the sample. The final pH, amount of base added, and the mass of the soil provided the lime buffer capacity of the soil (Kissel et al., 2012). Another study focused on determining a method to quickly estimate the lime buffer capacity of a soil by determining a typical reaction time required once a base is added to soils and finding a relationship between the pH measured after a fixed reaction time and the final pH that resulted after the extended reaction time. In that study, a base was added to several soil samples and allowed to react over differing reaction times. The study determined that the required reaction time to progress to equilibrium was approximately five days (Thompson et al., 2010). A third study looked at the addition of an acid to several clays to determine the soil's buffering capacity for the purposes of evaluating the potential for metals to leach from landfills lined with different clays (Phadungchewit, 1990). Phadungchewit took soil samples of each clay type, air-dried the samples, and ground the samples to pass a 2-millimeter (mm) sieve. The samples were then separated into 4-gram aliquots and added to plastic tubes. A fixed volume of nitric acid solution (40 mL or a 1:10 soil to solution mixture) was then added to each aliquot. The soil suspension was mixed for 24 hours, centrifuged for 10 minutes, and the pH was measured. Guidance for soil testing in Missouri (Nathan et. al., 2012) also recommends crushing soil samples to pass a 2 mm sieve and air-drying the soil samples at low heat (less than 85°F). In each study, various reaction times were provided, and the methods varied slightly.

For the purposes of measuring the soil buffering capacity for the pilot study, soil and groundwater samples will be collected during installation of the new injection well, as described in Section 4.2.1. Two soil types (SP and ML-SM) will be tested, based on soil types noted in boring logs for wells MW-43 and MW-54 and the observed distribution of high pH in the subsurface. As discussed previously, the high pH target area is located within the Shoreline Area in the vicinity of the southwest corner of the site, between 30 and 60 feet bgs. In well MW-44 and in push probes completed during the 2011 shoreline investigation, these depths correspond to a dark grey, poorly graded sand (SP) from approximately 30 to 45 feet bgs and a dark grey silt and silty sand mixture (ML-SM) from 45 to

65 feet bgs. As noted in the draft CMS Work Plan, it appears that the caustic soda, which is denser than the groundwater, sank to the lower confining layer just below the silt and silty sand layer, and has been in contact with the lower portion of the SP layer and the upper parts of the ML-SM layer. Based on these observations, soil samples will be collected from these two soil units in an area of high pH during new injection well and observation well installation. The SP and ML-SM soil samples will be tested for soil buffering capacity.

For each soil sample, gravel and other debris larger than 0.25 inch will be separated, as they will likely provide insignificant soil buffering capacity. To ensure that a homogeneous sample is created for each of the two soil samples, each sample will be oven-dried at 70 Celsius ($^{\circ}\text{C}$) to remove free moisture from the soil and limit removal of the water present in the soil sample. This temperature was recommended by a chemist from ALS Environmental to dry the soil within a reasonable time. The soils will be heated with periodic mixing until a change in weight of less than 1 percent is observed over 1 hour of consecutive readings. Once the samples have been effectively dried, the soils will be allowed to cool, and each sample will be crushed to pass through a 2 mm or smaller sieve to limit pore diffusion reaction kinetics during soil testing. Each soil sample will then be dried again in an oven at 70°C until two consecutive measurements indicate agreement within 1 percent or less. The two crushed and dried soil samples will then be tested for soil buffering capacity. Each soil sample will be thoroughly mixed to prepare a homogeneous sample. A series of sample aliquots for each soil type will be prepared for testing; varying doses of acid will be added to each aliquot so that the test series span the anticipated range of soil buffering capacity.

The soil buffer capacity testing will be completed in two stages. The first stage will consist of coarse testing to characterize the approximate soil buffering capacity. The second stage will more precisely characterize soil buffering capacity. The buffering capacity will be assessed by mixing soil samples with deionized water and reagent-grade sulfuric acid. Some of the second stage tests will also assess the effect of site groundwater on the test results.

For the first stage, it is assumed that the total soil buffering capacity of each soil type will be approximately 20 times the total alkalinity of the groundwater in equilibrium with the soil, as measured in groundwater samples collected in the vicinity of the soil samples (e.g., a groundwater alkalinity of 1,000 parts per million calcium carbonate [CaCO_3] equivalents would result in a maximum estimated soil buffering capacity of 2 percent by weight [CaCO_3 equivalents]). The first stage will test buffering capacity of the soils by dosing 0, 5, 10, 15, 20, and 25 times the groundwater alkalinity by weight, in order to estimate the maximum buffering capacity to be used in the second stage of testing. Once an upper bound for the acid dose required to neutralize each of the two soil types is obtained, the two soils will be tested for buffering capacity by spanning the range from a blank dose (only deionized

water) to the maximum acid dose obtained in the first stage multiplied by a 25 percent uncertainty factor (i.e., 1.25 times the maximum dose obtained in stage 1).

The samples for each soil type will be run in duplicate during stage 2 final buffering capacity testing to assess reproducibility. In order to evaluate the potential effects of site groundwater on the soil buffer test, four of the duplicate soil samples for each soil type will be mixed with groundwater collected from the new injection well instead of deionized water. The four samples using site groundwater in place of deionized water will evenly span the range of the acid additions (at 20, 40, 60, and 80 percent of the maximum dose obtained in stage 1). The results from the samples with groundwater added will be used to assess the effect of groundwater on neutralizing the soil and the potential reduction in measured soil buffering capacity as a result of silica precipitation. During both stages of soil buffering capacity testing, the aliquots will be mixed with the acid/deionized water mixture (or site groundwater/acid mixture for some of the stage 2 duplicate tests) for an extended reaction time to allow the acid to react with the soil. Residual acid concentrations will be measured to enable the quantity of acid that reacted with the soil to be determined, enabling the soil buffering capacity to be calculated.

In summary, the soil buffering capacity test procedure will be performed for each of the two soil types as described below.

Stage 1:

1. A total of six aliquots, each approximately equal by weight (e.g., 5 grams each), will be prepared from each crushed, dried soil sample, for a total of 12 aliquots to be tested.
2. The test series for each type of soil will include six aliquots dosed with an acid/deionized water mixture at 0 (blank sample), 5, 10, 15, 20, and 25 (acid equivalence as CaCO_3 by mass) times the alkalinity measured in groundwater from the new injection well, as described in Section 4.3.1.
3. Each aliquot will be placed into a sample bottle and mixed with equal volumes of a mixture of deionized water and standardized reagent grade sulfuric acid, so that the volume of the water/acid mixture is 10–20 times the soil mass (e.g., 100 mL total volume of a mixture of water and acid for a 5-gram soil aliquot).

The pH will be measured after mixing the blank soil aliquots for 1 hour to verify consistent pH readings and to obtain a baseline pH.

4. Each aliquot will then be continually mixed using a laboratory mixer, shaker, or equivalent method. Consistent with the required reaction time obtained by Thompson et al. (2010), soil samples will be mixed continuously for four days, and the pH from all of the six aliquots for each soil type will be measured.

5. The samples will then be mixed for another 24 hours and the pH of all six aliquots for each soil type will be measured again, giving a total of five days of reaction time. This process will be repeated on a daily basis until a change of less than 0.1 SU is observed in all six aliquots for each soil type.

The results from Stage 1 will be evaluated to identify the approximate total soil buffering capacity for each soil type. These results will be used to establish the acid doses for Stage 2 testing. The maximum dose for Stage 2 will be based on 125 percent of the soil buffering capacity determined from Stage 1.

Stage 2:

1. A total of 32 aliquots, each approximately equal by weight (e.g., 5 grams each) will be prepared from each crushed, dried soil sample for stage 2 testing (64 aliquots total for the two soil types).
2. Twenty-one of the soil sample aliquots for each soil type will be prepared for the primary soil buffering capacity testing. The test series will include one blank sample where no acid is added and 20 aliquots with equal incremental amounts of acid up to the maximum estimated soil buffering dose for Stage 2 testing.
3. Eleven aliquots for each soil type will be prepared as a duplicate of the primary test series. The duplicate series will consist of:
 - a. One blank duplicate sample and six duplicates at 10, 30, 50, 70, 90, and 100 percent of the maximum stage 1 soil buffering capacity.
 - b. Four duplicates mixed with site groundwater collected from the injection well instead of deionized water at 20, 40, 60, and 80 percent of the maximum Stage 2 soil buffering dose.
4. Each aliquot will be placed into a sample bottle and mixed with equal volumes of deionized water or a mixture of deionized water (or site groundwater, in the case of the four duplicates described in 3b) and standardized reagent grade sulfuric acid, so that the volume of the water/acid mixture is 10–20 times the soil mass (e.g., 100 mL total volume of a mixture of water and acid for a 5-gram soil aliquot). For the primary and duplicate test series, each aliquot will be dosed with standardized reagent grade sulfuric acid to evenly span the estimated range of soil buffering capacity, with aliquots dosed from 0 to 125 percent of the measured Stage 2 soil buffering dose.

The pH of each aliquot will be measured after mixing the blank soil aliquots for one hour to verify consistent pH readings and to obtain a baseline pH.

5. Each aliquot will then be continually mixed using a laboratory mixer, shaker, or equivalent method. Consistent with the required reaction time obtained by Thompson et al. (2010), soil samples will be mixed continuously for four days and the pH will be measured for 5 of the



21 aliquots for the primary series for each soil using the 0, 25, 50, 75, and 100 percent acid-dosed containers.

6. The aliquots will then be mixed for another 24 hours and the pH of the same five samples will be measured again, giving the samples five days of reaction time. This process will be repeated on a daily basis until a change of less than 0.1 SU is observed in all five samples for each soil type.

The final pH measurement in each of the aliquots and the initial acid doses will be evaluated to develop a buffering capacity curve for each soil type. The duplicate aliquots will be used to assess the reproducibility of the soil buffering capacity tests. The duplicates mixed with groundwater will be compared to the deionized water test results to evaluate the effects of the groundwater on the soil buffering capacity measurement.

The buffering capacity of the soil will be used to identify the total acid dose needed to fully neutralize the soil. This information is needed to estimate the total amount of CO₂ that must be delivered by an injection system. A plot of the number of moles of sulfuric acid normalized versus unit soil mass will be generated to characterize the acid equivalents that must be added to the soil to yield a resulting pH. The plot should be similar to a titration curve used to describe the alkalinity of water at different pH values. Based on the final pH, this plot will indicate the corresponding number of equivalents of acid per unit mass of soil required for neutralization of the soil. This will directly relate to the mass of CO₂ needed for neutralization; dissolved CO₂ will yield one equivalent per mole for neutralization to a final pH of 6.5 SU.

The measured soil buffering capacity will not provide information regarding the amount of time it would take for site soil to be neutralized. The rate of soil neutralization must be assessed in the field during pilot testing. Data collected and key findings from the bench study will be summarized in a regularly scheduled monthly progress report following data collection and evaluation. Bench testing results also will be evaluated relative to the field pilot study program for potential revisions or modifications. If appropriate, a technical meeting will be held with EPA to review the bench test results and discuss potential revisions to the field pilot study program.

4.4 FIELD PILOT STUDY TESTING AND MONITORING PLAN

The field pilot study test plan is designed to address the objectives discussed in Section 3. Testing will consist of injecting gaseous CO₂ into the injection well and observing changes in pressure, water levels, pH, temperature, and groundwater chemistry in the observation wells. These data will be used

to assess the ROI and to evaluate potential impacts of CO₂ neutralization on groundwater quality. Four phases of testing are planned:

1. Phase 1: Assess the relationships for injection pressure, injection rate, and the ROI;
2. Phase 2: Assess initial pH rebound;
3. Phase 3: Perform constant flow injection at the optimal rate and pulsed operation to assess anticipated full-scale operating conditions; and
4. Phase 4: Assess long-term pH rebound.

Prior to the start of Phase 1 injection testing; the site-specific Health and Safety Plan will be modified as appropriate with threshold levels and controls to prevent worker exposure to potential air contaminants. In addition, CO₂ concentrations in the vent gas and ambient air may be monitored for worker health and safety during Phase 1 active injections using a CO₂ gas meter.

During Phase 1, a range of injection pressures and the corresponding injection flow rates will be tested in the initial series of injection test runs to assess the effect of injection pressure on injection flow rate and the corresponding effects of different flow rates on the ROI. The effects of the different injection flow rates on CO₂ losses to the vadose zone will be assessed by measuring changes in groundwater TIC. The approximate mass estimates for CO₂ delivery and dissolution will be used to estimate the mass of CO₂ lost (in pounds) per pound of CO₂ delivered to the aquifer, as measured at the injection system manifold. The utilization efficiency is calculated as the percentage of CO₂ delivered to the aquifer and available for neutralization of the groundwater (i.e., the total quantity of CO₂ dissolved into groundwater measured by TIC analyses) divided by the total mass of CO₂ injected. It is expected that the vent well will not collect all CO₂ released to the vadose zone during injection. Injection flow rates that maximize the CO₂ utilization percentage and yielding an acceptable ROI will be considered optimal.

The Phase 1 test runs will start at low injection pressure and proceed to the maximum injection pressure, as discussed in Section 4.4.1. Each test run will include a period with no CO₂ injection to allow residual pockets of CO₂ in the saturated zone to dissolve into the groundwater prior to subsequent injection tests. After completing the initial series of test runs, Phase 2 will consist of an extended monitoring period with no CO₂ injection to evaluate pH rebound and changes in groundwater chemistry. After rebound is judged to be sufficient (as discussed in Section 4.4.2), Phase 3 injection testing will resume at the optimal flow rate determined in the initial injection testing runs. The final Phase 4 will assess the pH rebound rate and collect further information on changes in groundwater chemistry. Table 5 summarizes monitoring to be conducted during each phase of the field pilot study.



Prior to initiating Phase 1 injection testing, baseline groundwater chemistry and characterization samples will be collected from the injection well, the observation wells (including monitoring wells MW-53/MW-54 and MW-29), and the vent well, which has a screen that extends beneath the water table. Each sample will be analyzed for:

- Field parameters (unfiltered sample): pH, temperature, turbidity, conductivity, and oxidation reduction potential;
- Unfiltered sample: TSS and total alkalinity; and
- Field filtered sample: TDS, dissolved TIC, and dissolved silica.

The analyses to be performed for Phase 1 testing are listed in Table 5. Samples collected from MW-53, MW-54, IMW-A1-D, and the injection well will be analyzed for some select metals. These wells with the addition of the vent well will also be sampled for sulfide, and the cations and anions listed in Table 5. These samples will provide a baseline for water chemistry and concentrations of site metals anticipated to be affected by the neutralization of site groundwater for comparison to samples collected after CO₂ injection.

4.4.1 Phase 1 Testing: Evaluation of Injection Pressure and Flow Rates

The initial phase of injection testing will evaluate a range of injection pressures, the corresponding injection rates, and the resulting effect on the ROI for the injection well. Additionally, groundwater mounding in the vicinity of the injection well will be assessed. According to the *In-Situ Air Sparging Engineer Manual* (USACE, 2013), injection pressures should range between the minimum injection pressure, (i.e., the sum of the hydrostatic pressure at the top of the well screen and the formation entry pressure) and the maximum injection pressure that does not cause fracturing of the subsurface soils. For the site, the minimum pressure to inject into the new injection well adjacent to MW-53/MW-54 is approximately 17 pounds per square inch gauge (psig), and the maximum injection pressure (including a safety factor of 20 percent) is approximately 28 psig (calculations are included in Attachment A). Initial injection testing will assess this pressure range.

Each injection pressure tested will have a corresponding injection flow rate that will depend on well and aquifer characteristics. Injection pressures for CO₂ will be controlled by manually adjusting the pressure regulator shown on Drawing P&ID 01. The injection well will be pressurized with CO₂ by opening the primary injection valve (HV-2) and the injection well inlet valve (HV-3), as shown on Drawing P&ID 01. The CO₂ injection pressure will be adjusted by manually setting the pressure reducing regulator (PR-1), which will maintain a constant injection pressure. The injection pressure will be adjusted incrementally from 17 psig up to 28 psig in five increments (17, 20, 23, 26, and

28 psig) and the flow rate for each test run, as measured by FM-1, will indicate the flow rate and also totalize the CO₂ gas flow.

As shown on Drawing P&ID 01, each observation well will include a pressure indicator (either handheld or a transducer and data logger) that will be used to measure pressure in the well headspace to support evaluation of the ROI for each injection pressure being tested. In addition, each observation well will be equipped with a transducer/logger installed beneath the water level to measure and record water levels in order to evaluate groundwater mounding. It is anticipated that the pressure and water levels in the observation wells located within the ROI will increase after injection startup, will approach a semi-steady state, and then subside somewhat after gas channels have reached the vadose zone. As a result, the pressure and water level measurements being logged in the observation wells can be used as one indicator of the ROI and to determine optimal injection periods for pulsed operations (as defined by the increasing water levels and pressures in the observation wells). Groundwater pH and temperature in the wells will also be monitored using automated data loggers, and the results will be used to support evaluation of the ROI. The groundwater temperature logger will be used to assess the potential for exothermic effects during CO₂ injection.

Once a decline in pressure and water levels is observed in the observation wells, the constant pressure run will be judged complete and the CO₂ feed to the injection well will be closed off; the system will remain turned off for 24 hours to allow any excess CO₂ trapped in the aquifer to dissipate or dissolve. Pressure in the wellhead and water levels will be logged in the observation wells during the periods between active injections to determine how long it takes for the pressure and water levels to decrease during the groundwater mound collapse and reach a steady-state value, implying that the effects of groundwater mounding created by gas injection have dissipated. It is assumed that at least 8 hours of injection time will be provided for each injection test run, but actual time requirements will depend on field conditions and will be determined in the field.

At the conclusion of each injection pressure test run (i.e., after pressure and groundwater mounding in the observation wells has dissipated), groundwater samples will be collected from each observation well and the vent well and analyzed in the field for the field parameters—pH, temperature, turbidity, conductivity, and ORP—and in the laboratory for total alkalinity, dissolved TIC, TDS, and dissolved silica. In addition, at the end of Phase I testing, samples from observation wells will be analyzed for TSS and samples collected from MW-53, MW-54, IMW-A1-D, the injection well, and the vent well will be analyzed for sulfide, and the cations and anions listed in Table 5. Results for pH, alkalinity, and TIC will be used to assess the ROI for the injection pressure/flow rate tested. Results for TDS, TSS, and dissolved silica will be used to assess precipitation caused by neutralization of the high pH



groundwater. The injection flow rate, water levels, and other observations from each test run will be logged and used to evaluate the ROI for each injection pressure. In addition, groundwater pH and temperature will be logged in the pilot study observation wells and the vent well during and between test runs. Table 5 summarizes the monitoring to be performed for Phase 1 field testing.

4.4.2 Phase 2 Testing: pH and Water Chemistry Monitoring

Upon completion of the Phase 1 injection testing, pH rebound will be monitored during Phase 2 testing. The pH rebound and changes in groundwater chemistry caused by re-equilibration with the soil matrix will be assessed by monitoring pH in observation wells and the vent well and collecting groundwater samples at the end of Phase 2 from the pilot study observation, injection, and vent wells. The groundwater samples will be analyzed to monitor changes in groundwater chemistry resulting from CO₂ injection and re-equilibration. The Phase 2 groundwater samples will be analyzed for:

- Field parameters (unfiltered sample): pH, temperature, turbidity, conductivity, and oxidation reduction potential;
- Unfiltered sample: TSS and total alkalinity; and
- Field filtered sample: TDS, dissolved TIC, and dissolved silica.

Analyses to be performed for Phase 2 testing are listed in Table 5. Samples collected from MW-53, MW-54, IMW-A1-D, the injection well, and vent well will be analyzed for sulfide and the cations and anions listed in Table 5. These data will be used as appropriate to support Visual MINTEQ modeling runs in order to assess changes in groundwater chemistry; the modeling will include precipitation equilibria for amorphous silica. In addition, pH and temperature will be monitored in the observation wells to assess pH rebound and temperature changes from re-equilibrium of the neutralized groundwater with site soils. The data collected from the pH probes will be used to assess the rate of pH rebound and to determine when rebound monitoring should be terminated to proceed with Phase 3 injection testing.

During the Phase 2 monitoring period, the data collected during the Phase 1 initial injection testing will be evaluated. These results will be used to finalize plans for the full-scale injection testing to be conducted in Phase 3. The optimal injection flow rate will be identified from the results of the Phase 1 testing. The pH rebound, as measured in the injection well and the observation wells adjacent to the injection well (i.e., MW-53/MW-54 and observation well points "IMW A" or "IMW B" shown on Figure 6), will be assessed to determine when to commence Phase 3 testing. Rebound will be considered complete when the pH in these observation wells increases to 10 SU or greater. A pH of 10 SU was selected as wells MW-53/MW-54 have had historical pH measurements between 10 and 11 SU. The pH rebound target of 10 SU will be re-evaluated after completing bench testing. Revision

of the rebound pH target, if necessary, will be determined from this evaluation. Prior to the initiation of Phase 3 testing, results from Phases 1 and 2 and the final details for the Phase 3 testing plan will be summarized and submitted to EPA in the monthly progress report following completion of this work. Progress in the data evaluation will also be discussed in the monthly progress reports submitted to EPA. Phase 3 will be initiated following EPA review and acceptance of the results from Phases 1 and 2.

4.4.3 Phase 3 Testing: Full-Scale Injection Simulation

Phase 3 field testing will consist of full-scale injection simulations at the optimum injection rate, as identified from Phase 1 testing. This section provides a general outline for how the testing would be structured; final details for the Phase 3 program will be presented in the data summary for Phases 1 and 2 noted above in Section 4.4.2. The Phase 3 injection simulation will include testing pulse injections (i.e., periodic, constant flow injections) to promote mixing and CO₂ distribution in the injection zone. Phase 3 testing will be done at the target flow rate determined from the Phase 1 injection outlined in Section 4.4.1. For Phase 3 testing, the target CO₂ injection flow rate selected from Phase 1 results will be held constant and the actual injection pressure will be monitored and recorded during testing. Changes in injection pressure required to maintain flow will indicate changes in aquifer characteristics (e.g., an increase in required injection pressure to maintain a given injection rate may indicate aquifer plugging due to precipitation in the injection well sand pack or aquifer formation).

The goal of the Phase 3 injection simulations will be to create conditions where the groundwater will mix due to cycles of groundwater mounding. This will be done through pulsed CO₂ injections, whereby the CO₂ flow will periodically be cycled on and off. The flow of CO₂ will be controlled using a solenoid valve connected to an on/off timer set to the appropriate injection cycles (see Drawing P&ID 01). Injection pressure for the injection well will be monitored throughout this phase of testing to assess changes in injection pressure for maintaining the target CO₂ flow rate. Pressures measured in the injection well and the other observation wells will be used in conjunction with water levels and pH measurements in the observation wells to fine-tune injection cycling during Phase 3. Injection cycling will continue during Phase 3 testing until the pH measured in the adjacent observation wells reaches approximately the site background pH (e.g., the average value for wells outside of the affected high pH areas from Table 1) or 6.5 SU, at which point the CO₂ injection flow will be stopped by closing the pressure regulator manually. A pH of 6.5 SU was selected because this value is close to the site background pH and the proximity of this pH to the first dissociation constant for carbonic acid (i.e., $pK_1 = 6.3$). A pH endpoint of 6.5 SU is also consistent with results obtained from the LCP Chemical Site in Brunswick, Georgia (Mutch, 2013). This pH target may be adjusted based on results from bench testing and Phases 1 and 2, as noted above in Section 4.4.2.



Based on chemical equilibrium model results for groundwater collected from MW-44 (discussed in Section 2.0), it is estimated that it will take approximately 3,500 mg/L of CO₂ to neutralize the groundwater with an initial pH of 10.8 SU. Assuming a 20 percent utilization efficiency during field testing (similar to what was observed at the LCP Chemical site [Mutch, 2013]), an approximate mass loading of CO₂ of 17,500 mg/L would be required to dissolve sufficient CO₂ to meet neutralization objectives. Assuming a total porosity of 50 percent, as assumed in Attachment A, this would result in an approximate CO₂ mass loading of 2.2 pounds per cubic foot of aquifer. Assuming a CO₂ distribution in the aquifer in the shape of a cylinder with a radius of 25 feet and a total height of 50 feet, an estimated total mass of 110 tons of CO₂ would be required just to neutralize groundwater in this cylindrical volume. The mass of CO₂ required to meet neutralization objectives will be further evaluated based on results from the groundwater bench study, as discussed in Section 4.3, and baseline groundwater samples collected from the injection well, vent well, and observation wells. The total mass of CO₂ required also may be adjusted based on the measured ROI and preliminary utilization estimates from Phase 1 testing. It should also be noted that additional CO₂ will be required to neutralize affected soil, and that the CO₂ needed for soil neutralization will be delivered to the subsurface by dissolution into groundwater.

During injections for the full-scale Phase 3 testing pH, temperature, pressure, and water levels in all of the observation wells (including the vent well) will be logged for the duration of the testing. A complete groundwater chemistry analysis will be performed for all of the pilot study wells immediately after Phase 3 injections have ceased. The groundwater samples will be analyzed for:

- Field parameters (unfiltered sample): pH, temperature, turbidity, conductivity, and oxidation reduction potential;
- Unfiltered sample: TSS and total alkalinity; and
- Field filtered sample: TDS, dissolved TIC, and dissolved silica.
- Samples collected from MW-53, MW-54, IMW-A1-D, the vent well, and the injection well will be analyzed for sulfide, and the cations and anions listed in Table 5.
- Samples collected from MW-53, MW-54, IMW-A1-D, and the injection well will be analyzed for selected metals.

These samples will provide water chemistry and concentrations of the metals present at the site that may be affected by neutralization of site groundwater. The results from these samples will be

compared to samples collected in the field prior to CO₂ injection Table 5 shows a detailed summary of monitoring to be performed during Phase 3.

4.4.4 Phase 4 Testing: Rebound Monitoring

Upon completion of the Phase 3 injection testing, a second period of pH rebound monitoring will begin. During this rebound monitoring period, pH and temperature will be monitored using data loggers and/or manual monitoring in the observation wells adjacent to the injection well. Monitoring will continue until the pH of the groundwater in MW-53/MW-54 and/or in the adjacent observation wells has increased to approximately 10.0 SU or until pH monitoring data indicate that pH has stabilized and it is not likely that the groundwater pH in these observation wells will rebound to this pH level in a reasonable time period. Monitoring results will be summarized in monthly progress reports regularly submitted to EPA during the Phase 4 monitoring period. Pressure and water levels in the pilot study observation wells will be monitored after injections have ceased until steady state groundwater levels and pressures are observed, in order to evaluate how mounding effects change after an extended injection period.

At the end of Phase 4, samples will be collected from the observation wells and analyzed for:

- Field parameters (unfiltered sample): pH, temperature, turbidity, conductivity, and oxidation reduction potential;
- Unfiltered sample: TSS and total alkalinity; and
- Field filtered sample: TDS, dissolved TIC, and dissolved silica.
- Samples collected from MW-53, MW-54, IMW-A1-D, the vent well, and the injection well will be analyzed for sulfide, and the cations and anions listed in Table 5.
- Samples collected from MW-53, MW-54, IMW-A1-D, and the injection well will be analyzed for some limited metals.

These samples will provide water chemistry and concentrations of site metals that may be affected by the rebound of the neutralized site groundwater. The results will be compared to analytical results for samples collected during baseline groundwater sampling and samples collected after CO₂ injection is stopped. These groundwater samples will be collected once groundwater pH has stabilized. Table 5 shows a detailed summary of monitoring to be performed during Phase 4.



4.5 PROTECTIVENESS MONITORING

The site-specific Health and Safety Plan will be updated to address potential worker exposure and the hazards associated with the CO₂ pilot study. Action levels for CO₂ and other volatile site COCs will be addressed in the Health and Safety Plan, which will include monitoring and mitigation procedures.

4.6 SAMPLING

Samples of the two primary soil types present in the target area will be collected during the installation of the new injection well and observation wells for the CO₂ injection pilot field study. The boring for collection of soil samples will be done in an area with a high pH (more than 10.5 SU), as described in Section 4.1. After completion of the new injection well and observation wells, groundwater samples will be collected from MW-29, MW-53, MW-54, and the new observation wells to establish baseline conditions prior to initiating CO₂ injection. Samples will be collected as described in Section 4.4 and on Table 5 for the CO₂ injection runs and prior to pH rebound monitoring to compare neutralized water analyses to the baseline lab results and to the groundwater bench study testing results. In general soil and groundwater samples will be collected in accordance with the 2016 Quality Assurance Project Plan (QAPP) (Amec Foster Wheeler, 2016) but may not follow all of the requirements of the QAPP such as the requirements for data validation and field duplicates.

Table 5 summarizes monitoring to be performed during all phases of the field study.

4.7 PERMITTING

Subsurface injection permits will be obtained from the Washington State Department of Ecology prior to implementing CO₂ injections for the pilot study. Start cards will be obtained for installation of the injection well, the observation wells, and the vent well. Due to the low CO₂ injection rates anticipated for the pilot study (approximately 3-4 standard cubic feet per minute), it is not expected that Puget Sound Clean Air Agency (PSCAA) permitting will be required. Based on groundwater data collected in March and June of 2014 from the southwest corner of the Site (including MW-53/MW-54 and MW-29), the maximum groundwater concentrations observed for benzene, ethylbenzene, toluene, and xylene (BTEX) were 0.76 micrograms per liter (µg/L), 0.28 µg/L, 530 µg/L, and 1.35 µg/L, respectively. If it is assumed that all of the BTEX components in groundwater are present within a cylindrical area based on the ROI of the injection well (assuming a 50 foot ROI) and the entire depth of groundwater above the injection well screen (i.e., 40 feet), the maximum amount of BTEX that could possibly be emitted during CO₂ injections (assuming 100 percent removal from groundwater) is approximately 4.2 pounds of BTEX. Benzene accounts for less than 1 percent of this mass. Under PSCAA Article 6 Section 6.03(C)(94), soil and groundwater remediation projects involving less than 15 pounds per year of

benzene and less than 1,000 pounds per year of all toxic air contaminants are exempt from requirements for a Notice of Construction and Order of Approval.



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5.0 REPORTING

During the CO₂ pilot study, progress reports will be prepared and submitted to EPA and the USACE monthly along with the current monthly progress reports for the site. In addition to the data presented in the current monitoring reports, the monthly reports will include tables of the data collected or received during the preceding month and a summary of pilot study activities planned for the next reporting month. Significant issues or findings, if any, will be described in the progress reports. The monthly data summary will include the quantity of CO₂ injected, the duration of active injection and/or pH rebound evaluation, pH monitoring data, and typical injection pressures. A technical meeting may be held with EPA and the USACE as appropriate to discuss bench testing results or Phase I and Phase II results to finalize plans for field testing.

After completing CO₂ injection and pH rebound runs and obtaining the resulting analytical data as described above, a brief summary of results will be submitted to the EPA and USACE in a technical memorandum. A detailed summary Pilot Study Report documenting pilot study field methods, observations, results, conclusions, and recommendations will be prepared and submitted to the EPA as an attachment to the CMS. Deviations, if any, from this work plan will be documented in the Pilot Study Report. Data results will be summarized in tables and plots as appropriate. A final recommendation for the potential applicability and feasibility of CO₂ injections to neutralize soil and groundwater within the high pH target area will be presented in the CMS.



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6.0 SCHEDULE

A complete project schedule is included in the Section 10 of the CMS Work Plan. The schedule projects that the CO₂ pilot study will take approximately 37 weeks after EPA approval of the CMS Work Plan. The actual schedule may be changed, if appropriate, based on information collected during performance of the pilot study. Updates to the pilot study schedule will be included in the monthly progress reports.



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7.0 REFERENCES

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TABLE 1
GROUNDWATER pH MEASUREMENTS¹
 Former Rhone-Poulenc Site
 Tukwila, Washington

Monitoring Well ^{3,4}	pH (min) (SU)	pH (avg) (SU)	pH (max) ² (SU)
DM-7 ⁵	--	--	6.55
DM-8	6.50	6.69	6.85
H-10 ⁵	--	--	6.42
MW-12 ⁵	--	--	6.47
MW-17 ⁵	6.41	6.59	6.89
MW-20 ⁵	--	--	6.56
MW-27 ⁵	8.88	9.33	10.16
MW-28 ⁵	10.33	10.58	11.28
MW-29 ⁵	6.43	6.57	6.78
MW-51 ⁵	--	--	6.84
MW-52 ⁵	--	--	7.92
MW-53 ^{5,6}	7.48	--	10.79
MW-54 ^{5,6}	9.71	--	10.52
MW-38R	6.65	6.76	7.36
MW-39	6.80	7.33	7.64
MW-40	7.66	7.82	7.95
MW-41	8.60	9.72	10.24
MW-42	7.52	7.61	7.68
MW-43	9.02	10.68	11.36
MW-44	9.05	10.63	11.26
MW-45	7.03	7.40	7.84
MW-46	6.23	6.40	6.69
EX-3 ⁵	6.30	6.62	6.90
Push Probe⁷			
SL-07	--	--	8.86
SL-08	--	--	9.84
SL-09	--	--	10.24
SL-10	--	--	10.27
SL-11	--	--	10.62
SL-12	--	--	11.50
SL-13	--	--	10.68
SL-14	--	--	10.90
SL-15	--	--	9.82

Notes

1. **Bold** pH values are above the acceptable range for the Duwamish Waterway.
2. Maximum acceptable pH is 8.5, based on Washington State Department of Ecology surface water criteria for the Duwamish Waterway.
3. Monitoring well pH data includes all data from 2008–present.
4. For locations with fewer than three analyses, no average is calculated and only a min and max are shown. For locations with only one analysis, the result is presented as the maximum.
5. Analytical results include nonroutine samples collected in June 2014.
6. Analytical results include nonroutine samples collected in March 2014.
7. Push probe data are from the Shoreline Soil and Groundwater Characterization Data Report (AMEC, 2012). The data are the maximum for the probe locations.

Abbreviations

avg = average
 max = maximum
 min = minimum
 SU = standard unit

TABLE 2
PILOT STUDY WELLS pH, TOTAL ALKALINITY, AND TOTAL DISSOLVED SILICON
Former Rhone-Poulenc Site
Tukwila, Washington

Well ^{1,2,3}	pH (min) (SU)	pH (avg) (SU)	pH (max) (SU)	Total Alkalinity (min) (mg/L CaCO ₃)	Total Alkalinity (avg) (mg/L CaCO ₃)	Total Alkalinity (max) (mg/L CaCO ₃)	Silicon (min) (mg/L)	Silicon (avg) (mg/L)	Silicon (max) (mg/L)
HCIM Area Wells									
MW-29	6.43	6.57	6.78	234	280	427	40	44	46
MW-53	7.48	--	10.79	--	--	1,000	--	--	224
MW-54	9.71	--	10.52	--	--	1,030	--	--	3,870
Shoreline Area Wells									
MW-43	9.02	10.68	11.36	1,800	1,933	2,020	214	325	391
MW-44	9.05	10.63	11.26	2,540	2,718	2,980	628	643	667

Notes

1. For wells with less than three sample results, no average is calculated and only a min and max are shown. For wells with only one analysis, the result is presented as the maximum.
2. pH data are for groundwater monitoring and sampling from March 2008 to present.
3. Alkalinity and silicon data shown includes all 2005 data and samples collected for MW-29, MW-53 and MW-54 in 2014. No routine samples were collected for MW-53 or MW-54 for these analyses after 2005.

Abbreviations

avg = average

CaCO₃ = calcium carbonate equivalents

max = maximum

min = minimum

mg/L = milligrams per liter

SU = standard unit

HCIM =

TABLE 3
PERFORMANCE MONITORING ROUND 28 WATER CHEMISTRY DATA¹
 Former Rhone-Poulenc Site
 Tukwila, Washington

Well ID	Laboratory pH ²	Total Alkalinity (mg/L CaCO ₃)	Total Silicon (mg/L)	Cations					Anions				Total Metals					T _P (mg/L)	T _N (mg/L)
				Sodium (mg/L)	Potassium (mg/L)	Calcium (mg/L)	Magnesium (mg/L)	Iron (mg/L)	Cl ⁻ (mg/L)	SO ₄ ²⁻ (mg/L)	HS ⁻ (mg/L)	NO ₂ ²⁻ (mg-N/L)	Manganese (mg/L)	Vanadium (mg/L)	Chromium (mg/L)	Aluminum (mg/L)	Copper (mg/L)		
MW-28	10.58	1,460	320	476	26.3	4.38	0.45	5.6	12.5	122	4.01	0.125	0.178	0.047	0.010	0.89	0.069	2.30	0.125
MW-28 Dup	10.58	1,460	324	499	27.3	3.82	0.3	3.8	12.5	120	4.39	0.125	0.118	0.044	0.010	0.88	0.072	2.49	0.125
MW-38	6.72	342	30.5	107	5	17.9	18.7	21.5	35.9	165	0.05	0.05	1.060	0.032	0.007	0.37	0.006	1.95	0.05
MW-39	7.58	682	22.1	533	20.3	5.45	9.41	3.1	531	263	0.05	0.100	0.062	0.025	0.010	0.89	0.011	13.8	0.100
DM-5	7.34	1,430	24	509	5.3	13.8	10.8	10.6	53.2	576	0.05	0.25	0.147	0.457	0.112	3.06	0.026	18.6	0.25
MW-27	10.07	2,400	271	1,440	63.4	2.36	0.34	0.8	10	977	4.1	0.100	0.017	0.050	0.003	2.11	0.084	1.36	0.10
MW-29	6.68	234	43.5	64	3.6	19.7	10.1	27.0	10.0	65	0.050	0.100	1.810	0.003	0.003	0.15	0.003	0.932	0.47
MW-42	7.71	696	18.6	521	20	7.72	9.21	1.6	546	98	0.050	0.125	0.092	0.031	0.013	6.39	0.022	19.0	1.26
DM-8	6.96	256	25.7	330	8.0	19.2	9.11	13.0	232	435	0.050	0.125	1.430	0.059	0.009	0.89	0.013	6.24	0.125
MW-41	10.07	1,300	123	782	8.0	10.9	11.3	2.0	747	400	22.4	0.25	0.071	0.314	0.072	1.37	0.132	7.03	0.25
MW-41 Dup	10.11	1,330	126	875	8.4	11.5	11.1	2.1	724	383	19	0.25	0.071	0.359	0.076	1.44	0.139	8.32	0.25
MW-40	7.75	686	20.2	1,710	58.7	62.6	149	0.1	3650	102	1.18	0.025	0.118	0.008	0.003	0.49	0.016	15.00	0.025
MW-17	7.17	1,390	21.2	538	6.1	26.6	5.18	9.0	25	455	0.37	0.25	1.400	0.486	0.071	2.65	0.024	18.7	0.987
MW-43	10.34	2,020	336	939	18.9	11	0.32	1.8	411	451	7.5	0.25	0.010	0.390	0.074	1.21	0.044	29.6	0.526
MW-44³	10.98	2,980	668	859	8.3	8.44	1.36	6.8	74.3	161	14.5	0.125	0.196	0.310	0.033	1.21	0.131	1.84	0.125
MW-45	7.67	662	19.9	366	15.3	4.95	5.31	2.4	359	94	0.05	0.125	0.107	0.030	0.010	3.97	0.019	17.4	0.125
MW-46	6.5	391	26.3	219	13.9	58.1	37.7	34.0	365	27	0.05	0.05	1.240	0.011	0.003	0.05	0.002 U	1.08	0.05
EX-3	6.82	474	27.5	197	7.1	13.7	12.8	26.3	12.5	233	0.05	0.125	1.070	0.046	0.009	0.1	0.003	2.92	0.13
B1A	6.31	112	18.3	33	3.3	9.84	5.48	8.9	2.5	28	0.05	0.005	0.250	0.002	0.003	0.12	0.002 U	0.162	0.011

Notes

1. Round 28 sampling event data for samples collected June 14–16, 2005.
2. Laboratory pH was measured during alkalinity analysis for each sample.
3. **Bold** values were used in equilibrium model.

Abbreviations

CaCO ₃ = calcium carbonate equivalents	mg-N/L = milligrams as nitrogen per liter
Cl ⁻ = chlorine	NO ₂ ²⁻ = nitrite
Dup = Duplicate sample	SO ₄ ²⁻ = sulfate
HS ⁻ = bisulfide	T _N = Total nitrogen
mg/L = milligrams per liter	T _P = Total phosphorous

TABLE 4
CO₂ PILOT STUDY DATA QUALITY OBJECTIVES
 Former Rhone-Poulenc Site
 Tukwila, Washington

Pilot Study Component		Monitoring Point(s)	Medium	Objectives ¹	How Data are Intended to Meet the Objectives	Location Explanation
Aquifer Slug Testing	Baseline Testing	Injection well, MW 53, MW 54, and IMW-A1-D	GW	7	Falling head and rising head slug testing to estimate baseline hydraulic conductivity within the vicinity of the injection well to assess changes to hydraulic conductivity of saturated zone.	Locations selected within the immediate vicinity (10 feet) of the injection location. It is expected that measureable effects will be observed within the immediate vicinity of the injection well.
	Completion of Phase 3 Field Testing	Injection well, MW 53, MW 54, and IMW-A1-D	GW	7	Falling head and rising head slug testing after Phase 3 neutralization to assess changes in hydraulic conductivity due to CO ₂ injection.	
Bench Scale Testing	Groundwater Chemistry	Injection well	GW	1, 6, 7, 8	Groundwater titration with acid on representative groundwater sample to assess potential for solids precipitation/dissolution (changes in concentrations of TDS and silica). Groundwater alkalinity results will be compared to the model predictions discussed in Section 2 and may be used to adjust estimated CO ₂ mass requirements for field testing.	The injection well will be placed in the highest pH area expected to be encountered within the HCIM area and is expected to be representative of worst-case groundwater and soil. The injection well location is based on groundwater data from monitoring wells (i.e., MW-53 and MW-54) with characteristics similar to target areas outside the wall (i.e., MW-43 and MW-44). The distance from the barrier wall is based on the anticipated ROI and the likely injection well placement in the Shoreline Area if CO ₂ neutralization is selected in the CMS for implementation as part of the site remediation.
	Soil Buffering Capacity	Injection well	Soil	1	Soil buffering capacity, as measured through the change in pH in de-ionized water in contact with soil samples, will be used to estimate the acid demand to neutralize the aquifer matrix. The acid demand will be measured as an equivalence of acid required to neutralize a gram/kilogram of soil for the soil types tested. Based on this measurement and results from the field study for CO ₂ utilization efficiency, an estimate can be made for the total amount of CO ₂ , the number of injection events, and the time required to neutralize the aquifer matrix. It is anticipated that for each round of injection, high pH compounds from the soil matrix will diffuse into the groundwater and cause the groundwater pH to rebound until the source of the high pH in the aquifer matrix is exhausted.	
Field Testing	Phase 1	Injection well, MW 29, MW 53, and MW 54, All observation wells, Vent well	GW/Well Head	2, 3, 4, 6, 8	Phase 1 testing and monitoring are designed to provide information to assess the following: <ul style="list-style-type: none"> • The optimum injection flow rate (through measurements of influent CO₂ injection rates and pressures coupled with ROI measurements and utilization measurements); • The characteristics of the mound formation and collapse (as indicated by water level and pressure measurements in the observation wells) for various injection rates (which may be used in support of the final plan for Phase 3 testing); • The ROI (through well head pressure measurements, water levels, and TIC/alkalinity groundwater chemistry measurements [for changes in total carbonate species]); and • CO₂ utilization efficiency (through monitoring CO₂ injection volumes and changes in groundwater TIC and alkalinity to estimate the mass of CO₂ delivered and available for neutralization of groundwater). 	Observation wells and monitoring wells selected based on proximity to injection well. Depths selected based on injection depth and anticipated distribution of CO ₂ in the aquifer during injections.



TABLE 4
CO₂ PILOT STUDY DATA QUALITY OBJECTIVES
Former Rhone-Poulenc Site
Tukwila, Washington

Pilot Study Component	Monitoring Point(s)	Medium	Objectives ¹	How Data are Intended to Meet the Objectives	Location Explanation	
Field Testing Continued	Phase 2	Injection well, MW 29, MW 53, and MW 54, All observation wells, Vent well	GW	5, 8	Rebound monitoring during Phase 2 will include sample collection for general chemistry parameters to assess changes in geochemistry as a result of Phase 1 CO ₂ injections. In addition, pH rebound will be assessed by monitoring pH in the monitoring wells and observation wells during the rebound period and the data will be used to assess the kinetics of pH rebound to estimate neutralization time requirements.	The observation and monitoring wells monitored as part of Phase 2 are all within the anticipated ROI.
	Phase 3	Injection well, MW 29, MW 53, and MW 54, All observation wells, Vent well	GW/Well Head	1, 3, 4, 5, 6, 7, 8	Field injections during Phase 3 will help to assess the objectives outlined in Section 3.0 the Pilot Study Work Plan. The amount of CO ₂ required to be injected to neutralize high pH in the subsurface (soil and groundwater) may be assessed through mass balances on CO ₂ delivered to the aquifer and measured changes in TIC in groundwater samples upon meeting neutralization objectives described in Section 4.0. The estimated CO ₂ mass required for groundwater neutralization may be coupled with the total CO ₂ mass requirements for soil estimated from the bench testing to determine how many injection events may be required to meet neutralization objectives for the site (i.e., neutralization of both soil and groundwater). The ROI may be assessed based on changes in TIC/alkalinity measurements in the observation wells, water levels, and pressure readings in the well heads and refined from the Phase 1 approximation of the ROI; the ROI will be used in the CMS to estimate the number of wells required to neutralize the affected portions of the Shoreline Area. The characteristics of mound formation/collapse and effects of mounding on mixing and ROI during injections will be assessed by monitoring water levels and pressure readings in well heads and using TIC/alkalinity measurements from observation wells; these data will be used collectively to assess the ROI. Kinetics of pH neutralization may be evaluated by monitoring the rate of change in pH during active injections and during periods between active injections as CO ₂ dissolves in the groundwater; these data will be used to assess time required for neutralization. CO ₂ utilization efficiency may be estimated based on TIC/alkalinity measurements and the total mass of CO ₂ delivered to the aquifer; these data will be used to assess CO ₂ requirements. Analysis of post-injection groundwater samples may be used to assess changes in geochemistry from comparisons to baseline samples collected during Phase 1; these data will be used to assess changes in groundwater chemistry, including contaminant concentrations, caused by CO ₂ injection.	Observation wells and monitoring wells selected based on proximity to injection well. Depths selected based on injection depth and anticipated distribution of CO ₂ in the aquifer during injections.
	Phase 4	Injection well, MW 29, MW 53 and MW 54, All observation wells, Vent well	GW	5, 8	Rebound monitoring during Phase 4 will include sample collection for general chemistry parameters to assess changes in geochemistry as a result of pH rebound after Phase 3 CO ₂ neutralization injections have been completed. In addition, pH rebound will be assessed by monitoring pH in the monitoring wells and observation wells during the rebound monitoring period. The pH rebound data will be used in the CMS to estimate the time needed for neutralization of the Shoreline Area.	The observation and monitoring wells monitored as part of Phase 4 are all within the anticipated ROI.

Notes:

The objectives are as follows:

1. Estimate the amount of CO₂ that would be consumed to neutralize high pH groundwater and soil in contact with the high pH groundwater.
2. Assess CO₂ injection rates within the site.
3. Estimate the practical ROI for CO₂ injection wells.
4. Evaluate the formation and collapse of groundwater mounding caused by injection of gaseous CO₂.
5. Evaluate the kinetics of high pH groundwater neutralization and pH rebound.
6. Evaluate the CO₂ utilization efficiency and CO₂ consumption to neutralize high pH groundwater and soil in the field.
7. Evaluate potential changes in aquifer characteristics that may result from CO₂ injection.
8. Evaluate changes in geochemistry and other parameters that may result from CO₂ injection.

Abbreviations:

- CMS = Corrective Measures Study
- CO₂ = carbon dioxide
- GW = groundwater
- HCIM = hydraulic control interim measure
- ROI = radius of influence
- TDS = Total Dissolved Solids
- TIC = total inorganic carbon



TABLE 5
CO₂ INJECTION FIELD STUDY MONITORING PLAN
Former Rhone-Poulenc Site
Tukwila, Washington

Monitoring Event	Monitoring Location	Media	Pressure Gauge/ Transducer	Water Levels Transducer/ Manual	Field Parameters ¹	Temperature and pH ²	Alkalinity	Total Suspended Solids	Total Dissolved Solids ³	Total Metals ⁴	Dissolved Metals ^{3,5}	Dissolved Silica ³	Dissolved Total Inorganic Carbon ^{3,6}	Anions ⁷	Cations ⁸	Sulfide
Analytical Method					field sampler	lab or field probe	SM 2320 B-97	SM 2540	SM 2540	EPA 6020	EPA 6020	EPA 6020	SM 5310B	EPA 300.0	EPA 6010	
Bottle requirements			--	--	--	--	500 mL HDPE ⁹	1 L HDPE	1 L HDPE	500 mL HDPE	500 mL HDPE	500 mL HDPE	40-mL vial ⁹	500 mL HDPE	500 mL HDPE	500 mL HDPE ⁹
Preservative			--	--	--	--	<6°C	<6°C	<6°C	pH < 2 with 1:1 HNO ₃ ; <6°C	pH < 2 with 1:1 HNO ₃ ; <6°C	pH < 2 with 1:1 HNO ₃ ; <6°C	<6°C	<6°C	pH < 2 with 1:1 HNO ₃ ; <6°C	2 mL 1N Zinc acetate + 1 mL 10N NaOH pH>9
Hold Time			--	--	--	--	14 days	7 days	7 days	6 months	6 months	6 months	28 days	48 hours	6 months	7 days
Reporting Limit Goals ¹⁰			--	--	--	--	1 mg/L CaCO ₃	1 mg/L	5 mg/L	-	-	0.06 mg/L	0.5 mg/L	0.1 mg/L	-	0.05 mg/L
Aquifer Slug Testing Baseline	Injection Well	GW	X	X												
	IMW-A1-D	GW	X	X												
	MW-53	GW	X	X												
	MW-54	GW	X	X												
Groundwater Chemistry Bench Study	Injection Well-Baseline	GW			X	X	X	X	X			X				
	Neutralized Groundwater	GW				X	X	X	X			X				
Field Pilot Study Phase 1 Baseline Testing	Injection Well	GW			X	X	X	X	X	X	X	X	X	X	X	X
	IMW-A1-D	GW			X	X	X	X	X	X	X	X	X	X	X	X
	IMWs	GW			X	X	X	X	X			X	X			
	MW-29	GW			X	X	X	X	X			X	X			
	MW-53	GW			X	X	X	X	X	X	X	X	X	X	X	X
Field Pilot Study - Phase 1	MW-54	GW			X	X	X	X	X	X	X	X	X	X	X	X
	Vent Well	GW			X	X	X	X	X			X	X	X	X	X
Injection Run Monitoring	IMWs	GW	X	X		X										
	MW-29	GW	X	X		X										
	MW-53	GW	X	X		X										
Post Injection (each pressure) Monitoring	MW-54	GW	X	X		X										
	Vent Well	GW		X		X										
	IMWs	GW			X	X	X	X	X			X	X	X	X	X
Field Pilot Study - Phase 1 Post Injection	IMW-A1-D	GW			X	X	X	X	X			X	X	X	X	X
	IMWs	GW			X	X	X	X	X			X	X			
	MW-29	GW			X	X	X	X	X			X	X			
	MW-53	GW			X	X	X	X	X			X	X	X	X	X
	MW-54	GW			X	X	X	X	X			X	X	X	X	X
	Vent Well	GW			X	X	X	X	X			X	X	X	X	X



TABLE 5
CO₂ INJECTION FIELD STUDY MONITORING PLAN
Former Rhone-Poulenc Site
Tukwila, Washington

Monitoring Event	Monitoring Location	Media	Pressure Gauge/ Transducer	Water Levels Transducer/ Manual	Field Parameters ¹ field sampler	Temperature and pH ² lab or field probe	Alkalinity SM 2320 B-97	Total Suspended Solids SM 2540	Total Dissolved Solids ³ SM 2540	Total Metals ⁴ EPA 6020	Dissolved Metals ^{3,5} EPA 6020	Dissolved Silica ³ EPA 6020	Dissolved Total Inorganic Carbon ^{3,6} SM 5310B	Anions ⁷ EPA 300.0	Cations ⁸ EPA 6010	Sulfide SM 4500-S2
Analytical Method			Transducer	Manual	field sampler	lab or field probe	SM 2320 B-97	SM 2540	SM 2540	EPA 6020	EPA 6020	EPA 6020	SM 5310B	EPA 300.0	EPA 6010	SM 4500-S2
Bottle requirements			--	--	--	--	500 mL HDPE ⁹	1 L HDPE	1 L HDPE	500 mL HDPE	500 mL HDPE	500 mL HDPE	40-mL vial ⁹	500 mL HDPE	500 mL HDPE	500 mL HDPE ⁹
Preservative			--	--	--	--	<6°C	<6°C	<6°C	pH < 2 with 1:1 HNO ₃ ; <6°C	pH < 2 with 1:1 HNO ₃ ; <6°C	pH < 2 with 1:1 HNO ₃ ; <6°C	<6°C	<6°C	pH < 2 with 1:1 HNO ₃ ; <6°C	2 mL 1N Zinc acetate + 1 mL 10N NaOH pH>9
Hold Time			--	--	--	--	14 days	7 days	7 days	6 months	6 months	6 months	28 days	48 hours	6 months	7 days
Reporting Limit Goals ¹⁰			--	--	--	--	1 mg/L CaCO ₃	1 mg/L	5 mg/L	-	-	0.06 mg/L	0.5 mg/L	0.1 mg/L	-	0.05 mg/L
Field Pilot Study - Phase 2 Rebound Monitoring	IMWs	GW				X										
	MW-29	GW				X										
	MW-53	GW				X										
	MW-54	GW				X										
	Vent Well	GW				X										
Field Pilot Study - Phase 2 Post Rebound	Injection Well	GW			X		X	X	X			X	X	X	X	X
	IMW-A1-D	GW			X		X	X	X			X	X	X	X	X
	IMWs	GW			X		X	X	X			X	X			
	MW-29	GW			X		X	X	X			X	X			
	MW-53	GW			X		X	X	X			X	X	X	X	X
	MW-54	GW			X		X	X	X			X	X	X	X	X
	Vent Well	GW			X		X	X	X			X	X	X	X	X
Field Pilot Study - Phase 3 Pulsed Injection Run Monitoring	Injection Manifold	Gas	X													
	IMWs	GW	X	X		X										
	MW-29	GW	X	X		X										
	MW-53	GW	X	X		X										
	MW-54	GW	X	X		X										
	Vent Well	GW	X	X		X										
Field Pilot Study - Phase 3 Post Injection Monitoring	Injection Well	GW			X		X	X	X	X	X	X	X	X	X	X
	IMW-A1-D	GW			X		X	X	X	X	X	X	X	X	X	X
	IMWs	GW			X		X	X	X			X	X			
	MW-29	GW			X		X	X	X			X	X			
	MW-53	GW			X		X	X	X	X	X	X	X	X	X	X
	MW-54	GW			X		X	X	X	X	X	X	X	X	X	X
	Vent Well	GW			X		X	X	X			X	X	X	X	X
Aquifer Slug Testing Post Injections	Injection Well	GW	X	X												
	IMW-A1-D	GW	X	X												
	MW-53	GW	X	X												
	MW-54	GW	X	X												
Field Pilot Study - Phase 4 Rebound Monitoring	IMWs	GW	X ¹¹	X ¹¹		X										
	MW-29	GW	X ¹¹	X ¹¹		X										
	MW-53	GW	X ¹¹	X ¹¹		X										
	MW-54	GW	X ¹¹	X ¹¹		X										
	Vent Well	GW	X ¹¹	X ¹¹		X										

TABLE 5
CO₂ INJECTION FIELD STUDY MONITORING PLAN
 Former Rhone-Poulenc Site
 Tukwila, Washington

Monitoring Event	Monitoring Location	Media	Pressure Gauge/ Transducer	Water Levels Transducer/ Manual	Field Parameters ¹ field sampler	Temperature and pH ² lab or field probe	Alkalinity SM 2320 B-97	Total Suspended Solids SM 2540	Total Dissolved Solids ³ SM 2540	Total Metals ⁴ EPA 6020	Dissolved Metals ^{3,5} EPA 6020	Dissolved Silica ³ EPA 6020	Dissolved Total Inorganic Carbon ^{3,6} SM 5310B	Anions ⁷ EPA 300.0	Cations ⁸ EPA 6010	Sulfide SM 4500-S2
Analytical Method			--	--	--	--	500 mL HDPE ⁹	1 L HDPE	1 L HDPE	500 mL HDPE	500 mL HDPE	500 mL HDPE	40-mL vial ⁹	500 mL HDPE	500 mL HDPE	500 mL HDPE ⁹
Bottle requirements			--	--	--	--	500 mL HDPE ⁹	1 L HDPE	1 L HDPE	500 mL HDPE	500 mL HDPE	500 mL HDPE	40-mL vial ⁹	500 mL HDPE	500 mL HDPE	500 mL HDPE ⁹
Preservative			--	--	--	--	<6°C	<6°C	<6°C	pH < 2 with 1:1 HNO ₃ ; <6°C	pH < 2 with 1:1 HNO ₃ ; <6°C	pH < 2 with 1:1 HNO ₃ ; <6°C	<6°C	<6°C	pH < 2 with 1:1 HNO ₃ ; <6°C	2 mL 1N Zinc acetate + 1 mL 10N NaOH pH>9
Hold Time			--	--	--	--	14 days	7 days	7 days	6 months	6 months	6 months	28 days	48 hours	6 months	7 days
Reporting Limit Goals¹⁰			--	--	--	--	1 mg/L CaCO ₃	1 mg/L	5 mg/L	-	-	0.06 mg/L	0.5 mg/L	0.1 mg/L	-	0.05 mg/L
Field Pilot Study - Phase 4	Injection Well	GW			X		X	X	X	X	X	X	X	X	X	X
	IMW-A1-D	GW			X		X	X	X	X	X	X	X	X	X	X
	IMWs	GW			X		X	X	X		X	X				
Post-Neutralization Monitoring	MW-29	GW			X		X	X	X			X	X			
	MW-53	GW			X		X	X	X	X	X	X	X	X	X	X
	MW-54	GW			X		X	X	X	X	X	X	X	X	X	X
	Vent Well	GW			X		X	X	X			X	X	X	X	X

Notes:

- Field parameters include pH, temperature, turbidity, conductivity, and oxidation reduction potential.
- Continuous lab or field measurements.
- Samples will be filtered and method required preservation will be added prior to analysis.
- Total metals include: aluminum, arsenic, chromium, copper, iron, lead, manganese, and vanadium.
- Dissolved metals include: aluminum, arsenic, chromium, copper, iron, lead, manganese, and vanadium.
- Samples will initially be analyzed for total carbon, and then the sample will be purged and measured for total organic carbon, giving the total inorganic carbon result by subtraction.
- Anions include chloride, sulfate, and phosphate.
- Cations include sodium, calcium, potassium, magnesium, aluminum, and iron.
- No headspace.
- Analytical methods may be adjusted at the time of analysis to achieve reporting limits less than or equal to site Preliminary Remediation Goals established by EPA.
- Monitored until levels reach a steady state.

Abbreviations:

- = not applicable
- °C = degrees Celsius
- CaCO₃ = calcium carbonate
- EPA = Environmental Protection Agency
- GW = groundwater
- HDPE = high density polyethylene
- HNO₃ = nitric acid
- L = liter
- mg/L = milligrams per liter
- mL = milliliter
- N = normal
- NaOH = sodium hydroxide
- SM = Standard Method

TABLE 6
PILOT STUDY AREA AND HIGH pH SHORELINE AREA WELL DETAILS
Former Rhone-Poulenc Site
Tukwila, Washington

Well	Depth of Well ^{1,2} (feet bgs)	Screen Length ³ (feet)	Well Diameter (inches)	Distance from Injection Well (feet)	Vertical Distance from Injection Well Screen ⁴ (feet)
Shoreline Area High pH Wells					
MW-43	61.3	10	2	45	-16
MW-44	41.6	10	2	43	3
Pilot Study Injection Wells					
Injection Well	50	5	2	--	--
Pilot Study Observation Wells					
IMW A1-D	50	5	2	10	-5
IMW B1-S	35	10	2	20	10
IMW B1-D	50	5	2	20	-5
IMW C1-S	27.5	10	2	30	18
IMW A2-S	35	10	2	10	10
IMW A2-D	50	5	2	10	-5
IMW B2-S	27.5	10	2	20	18
MW-29	21.1	15	2	31	24
MW-53	40	10	2	7	5
MW-54	60	10	2	10	-15
Vent Well	25	15	2	10	20

Notes

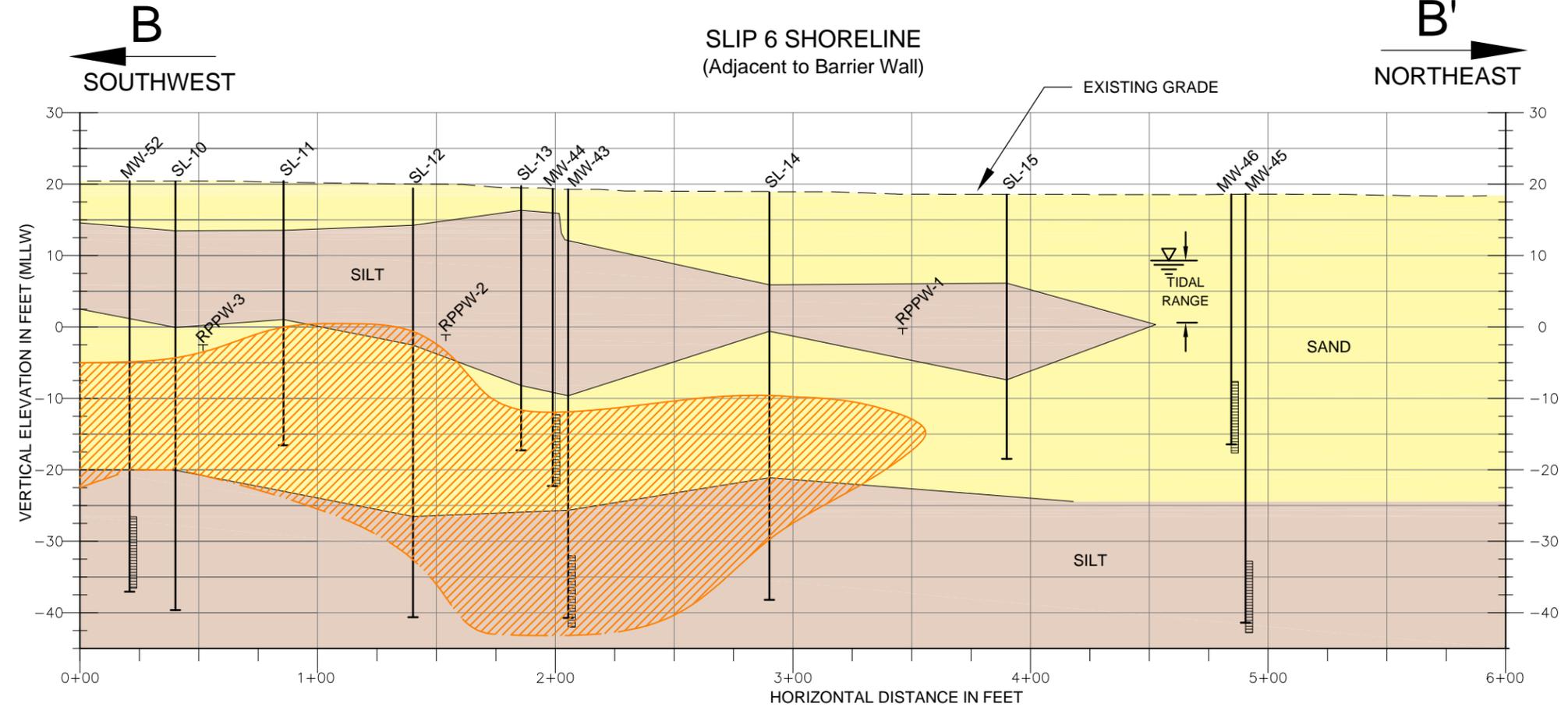
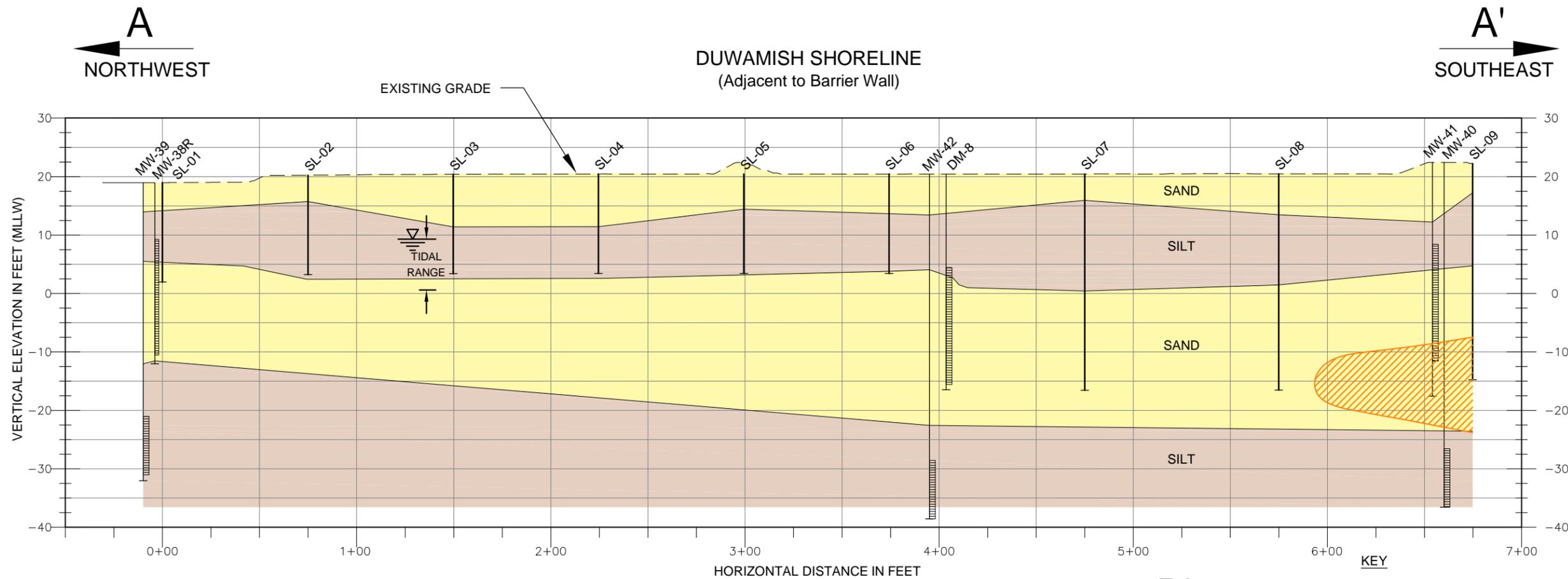
1. Depth of new injection, observation, and vent wells may be adjusted in the field depending on subsurface geology and chemistry.
2. Depth to bottom of well is the total depth from the ground surface to the bottom of the well's screen.
3. Screen length is the total length of the well screen.
4. Vertical distance from well screen is the difference in elevation from the top of the new proposed injection well screen (Figure 7) to the bottom of the designated well. A negative value means that the bottom of the designated well is deeper than the top of the new injection well screen.

Abbreviations

bgs = below ground surface

FIGURES

Plot Date: 09/12/16 - 1:15pm, Plotted by: adam.stenberg
 Drawing Path: S:\8769_2006\112_CMS Work Plan\CAD\ Drawing Name: FRP_SiteMap-pH_120915.dwg



KEY

- RPPW-1 POREWATER SAMPLING LOCATION PROJECTED ONTO THE LINE OF CROSS SECTION.
- WELL SCREEN INTERVAL
- SAND
- SILT
- SOILS AFFECTED BY CAUSTIC EXCEEDING 8.5 STANDARD UNITS

NOTE:

- LITHOLOGY SHOWN TO APPROXIMATELY DELINEATE BETWEEN SOIL TYPES.
- EXTENT OF HIGH pH CONTAMINATION SHOWN IS GENERALIZED TO REPRESENT THE APPROXIMATE EXTENT OF SOIL, SEDIMENT, AND GROUNDWATER CONTAMINATION FOUND AT THE SITE.
- LOCATIONS OF CROSS SECTIONS ARE SHOWN ON FIGURE 1.

APPROXIMATE SCALE IN FEET
 VERTICAL EXAGGERATION = 3X

**DUWAMISH AND SLIP 6 SHORELINE
 CROSS SECTION pH CONTAMINATION SUMMARY**
 Former Rhone-Poulenc Site
 Tukwila, Washington

By: APS	Date: 09/12/16	Project No. 08769
Amec Foster Wheeler Environment & Infrastructure, Inc.		Figure 2



Figure 3: MW-44 pH and Silicon Trend Data

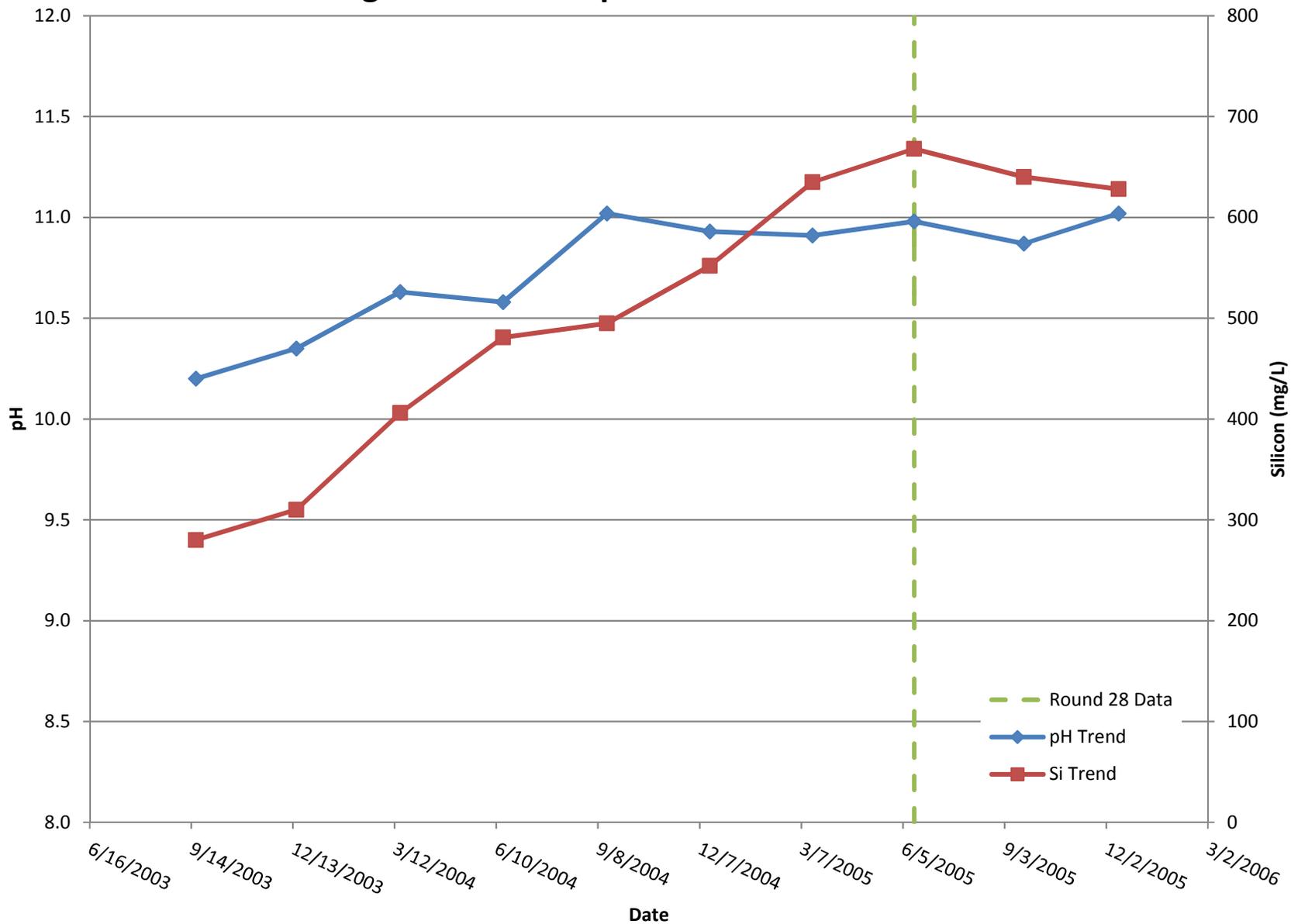


Figure 4: Total SiO₂ vs pH in Shoreline Area Groundwater

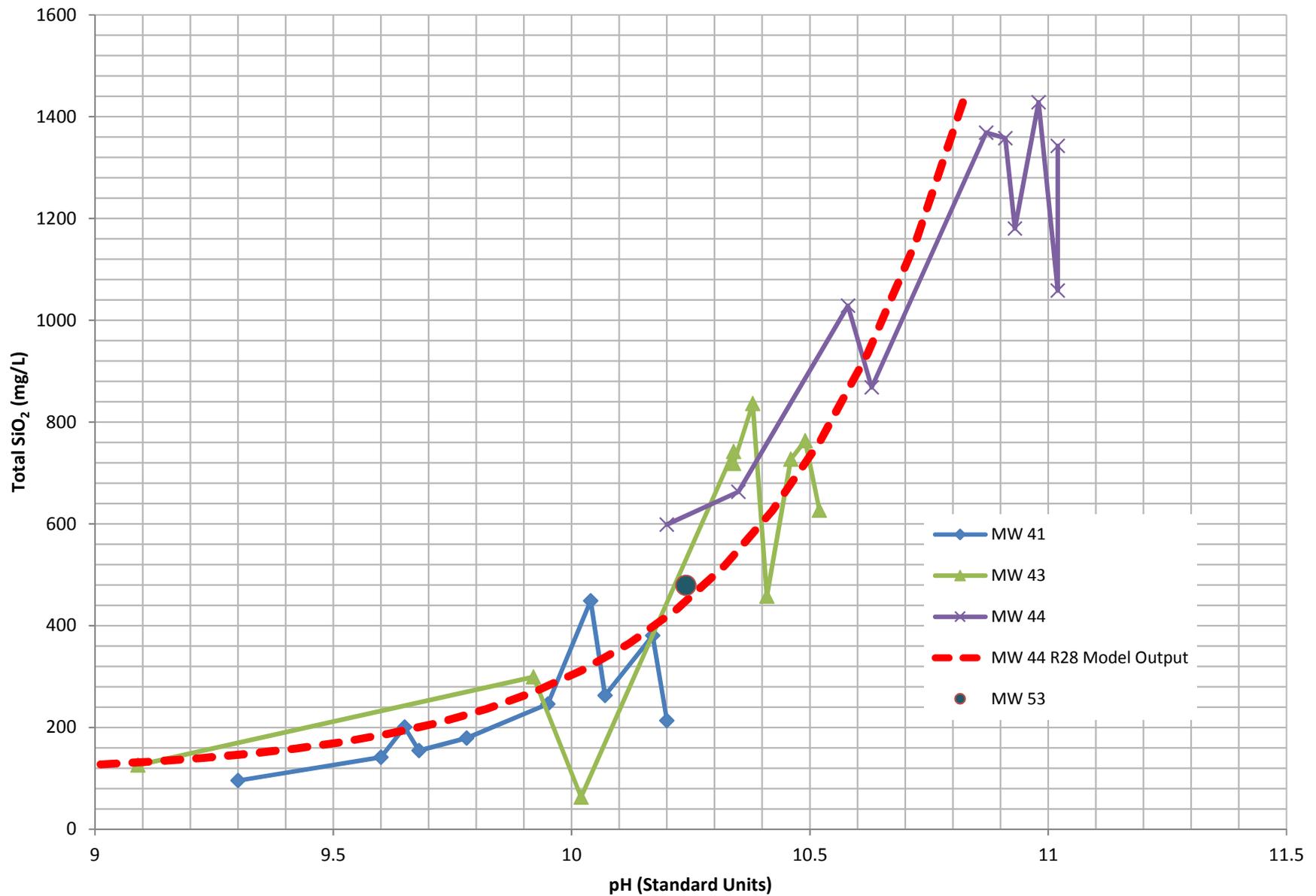
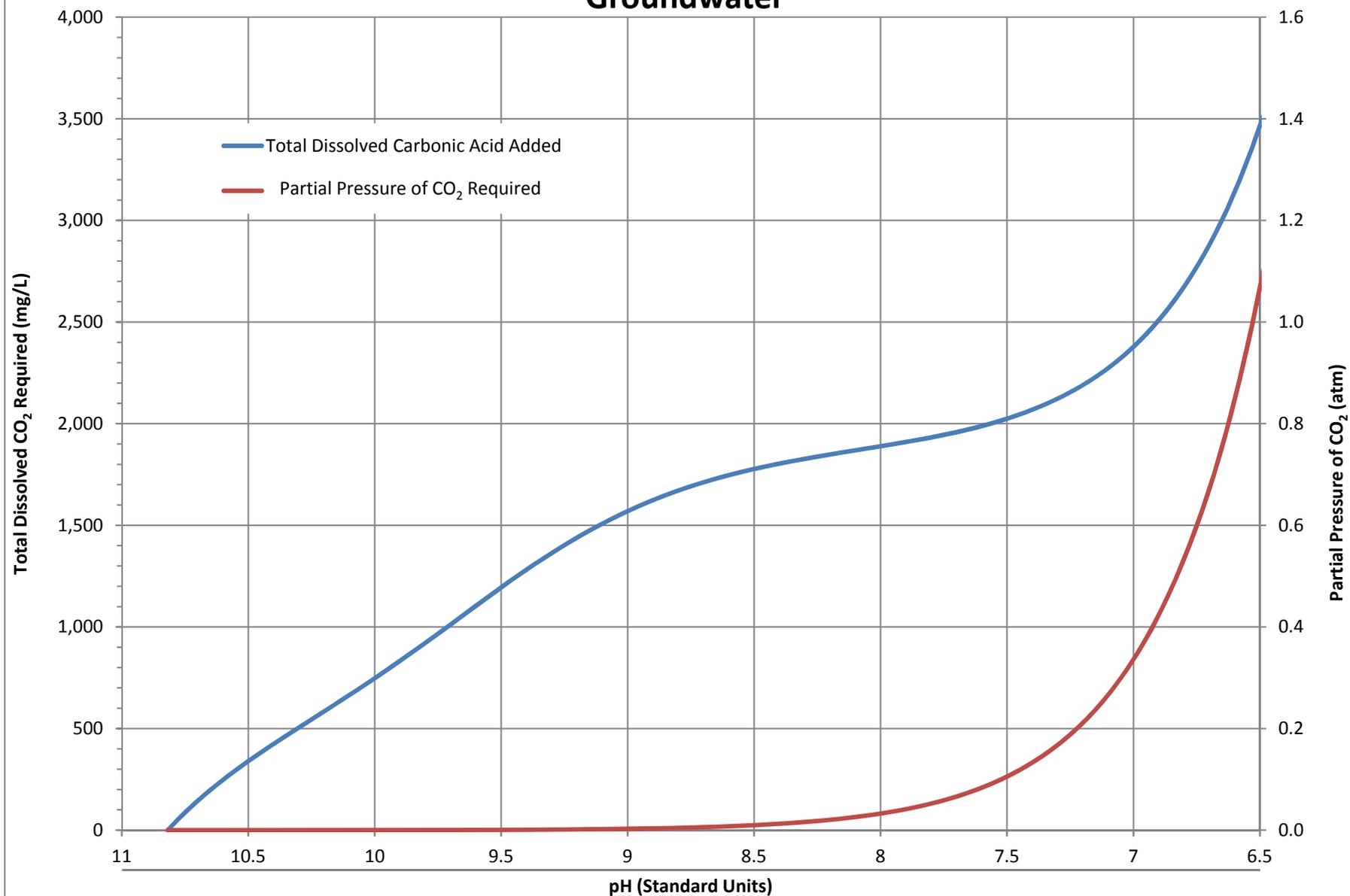
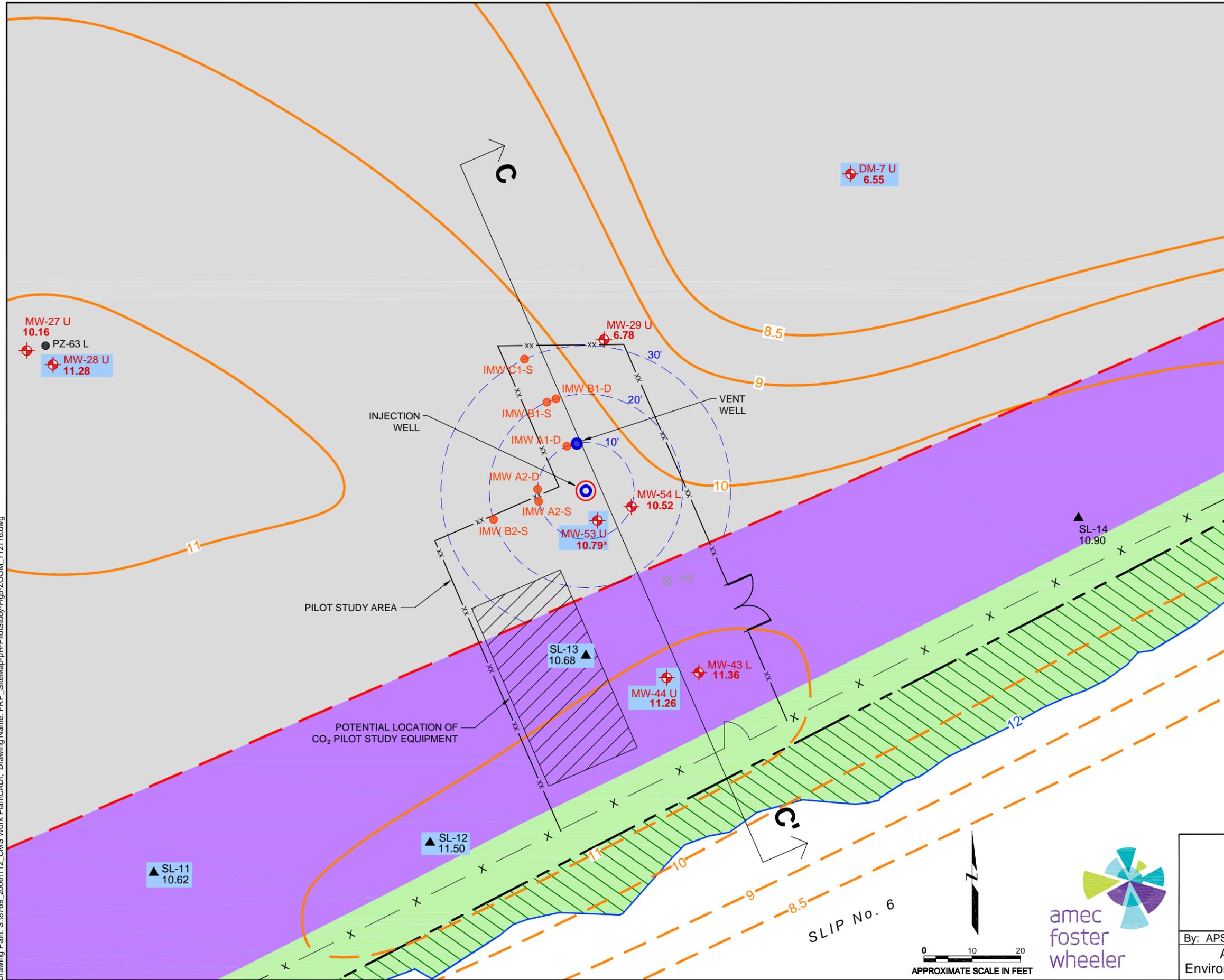


Figure 5: Predicted Total CO₂ Required to Reduce pH in Shoreline Area Groundwater



Plot Date: 11/21/16 - 12:52pm, Plotted by: adam.stenberg
 Drawing Path: S:\8769_2006\112_CMS Work Plan\CAD\ Drawing Name: FRP_SiteMap-pH-PilotStudy-Fig5-ZOOM_112116.dwg



EXPLANATION

- PROPERTY LINE
- - - - - APPROXIMATE LOCATION OF BARRIER WALL
- x - FENCE
- xx - TEMPORARY FENCING
- 12— ELEVATION CONTOUR (MLLW)
- ▲ SL-11 SHORELINE AREA GROUNDWATER SAMPLING LOCATION, 2011
10.62
- 11 GROUNDWATER pH CONTOUR (DASHED WHERE INFERRED)
- MW-45 L HIGHLIGHTED SAMPLE LOCATIONS USED TO GENERATE pH CONTOURS
7.34
- MW-54 L pH VALUE IS MAXIMUM OBSERVED FROM MARCH 2008 TO PRESENT
10.52
- * VALUE TAKEN FROM ALKALINITY MEASUREMENT INITIAL pH.
- IMW A1 PROPOSED CO₂ INJECTION MONITORING WELL
- PROPOSED CO₂ INJECTION VENT WELL

MONITORING WELL NETWORK

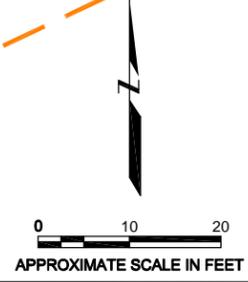
- ⊕ MONITORING WELL LOCATION
- U UPPER ZONE MONITORING POINT
- L LOWER ZONE MONITORING POINT
- S SHALLOW MONITORING POINT
- D DEEP MONITORING POINT

KEY

- ▭ HCIM AREA
- ▭ SHORELINE AREA
- ▭ PAVED SHORELINE AREA
- ▭ SLIP 6 SHORELINE AREA OWNED BY THE BOEING COMPANY

PILOT STUDY MONITORING AND INJECTION WELL LAYOUT
 Former Rhone-Poulenc Site
 Tukwila, Washington

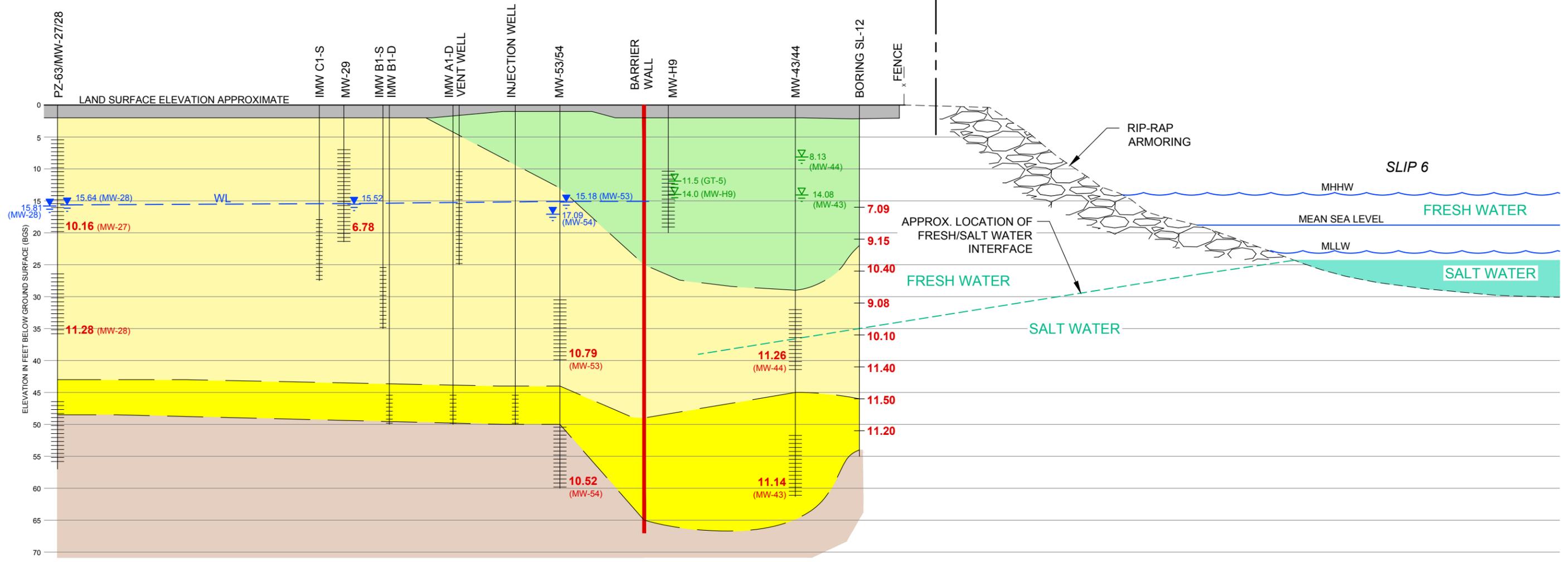
By: APS	Date: 11/21/16	Project No. 08769
Amec Foster Wheeler Environment & Infrastructure, Inc.		Figure 6



SLIP No. 6

C
← NORTH

C'
→ SOUTH



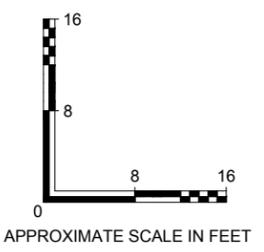
CROSS SECTION C-C'

KEY:

- PAVEMENT
- SILT AQUITARD
- WATER TABLE INSIDE BARRIER WALL
- WATER TABLE OUTSIDE BARRIER WALL
- APPROXIMATE LOCATION OF SALT WATER WEDGE BASED ON SOIL INVESTIGATION AND GROUNDWATER DATA
- WELL SCREEN INTERVAL
- IMW INJECTION MONITORING WELL
- 6.78 pH MEASUREMENT (STANDARD UNITS)

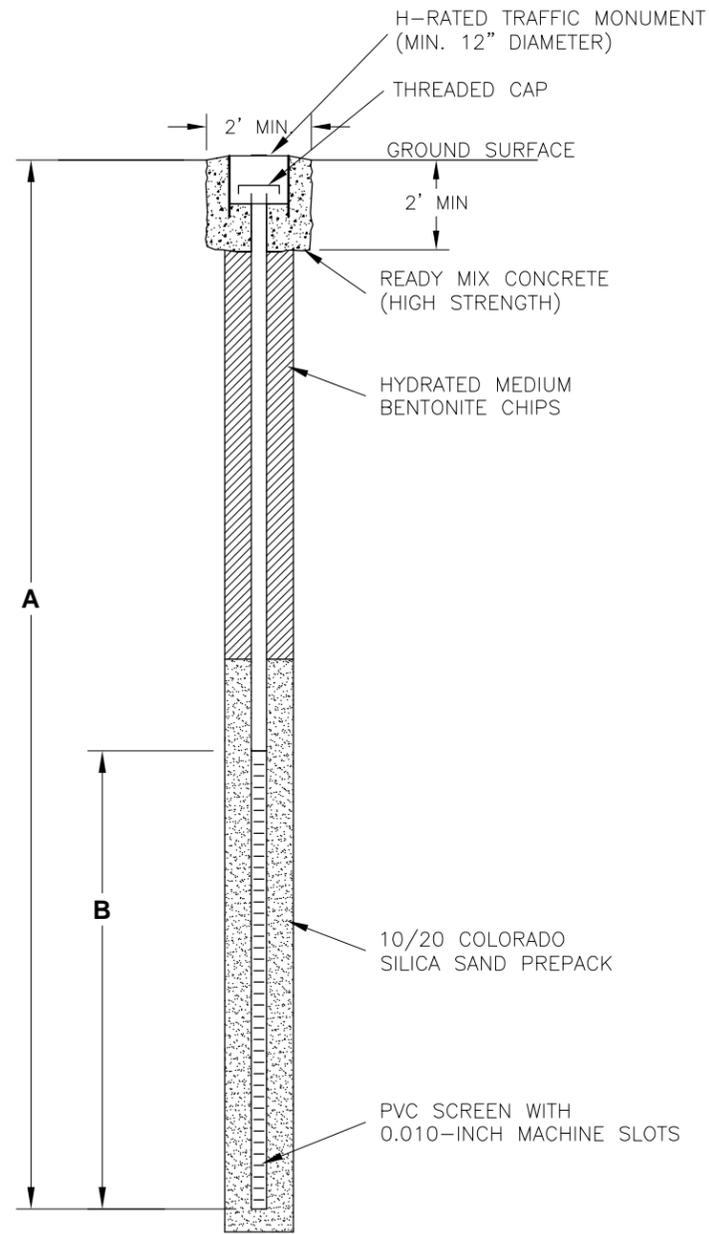
- UPPER AQUIFER ZONE**
 - SAND / SILT / SILTY SAND / CLAY
 - SAND (SP)
- LOWER AQUIFER ZONE**
 - SILTY SAND (ML-SM)

- NOTES:**
- WELL pH VALUES ARE MAXIMUM OBSERVED FROM MARCH 2008 TO PRESENT. SL-12 pH DATA IS FROM 2011 SHORELINE INVESTIGATION DATA.
 - CROSS SECTION LOCATION SHOWN OF FIGURE 6.

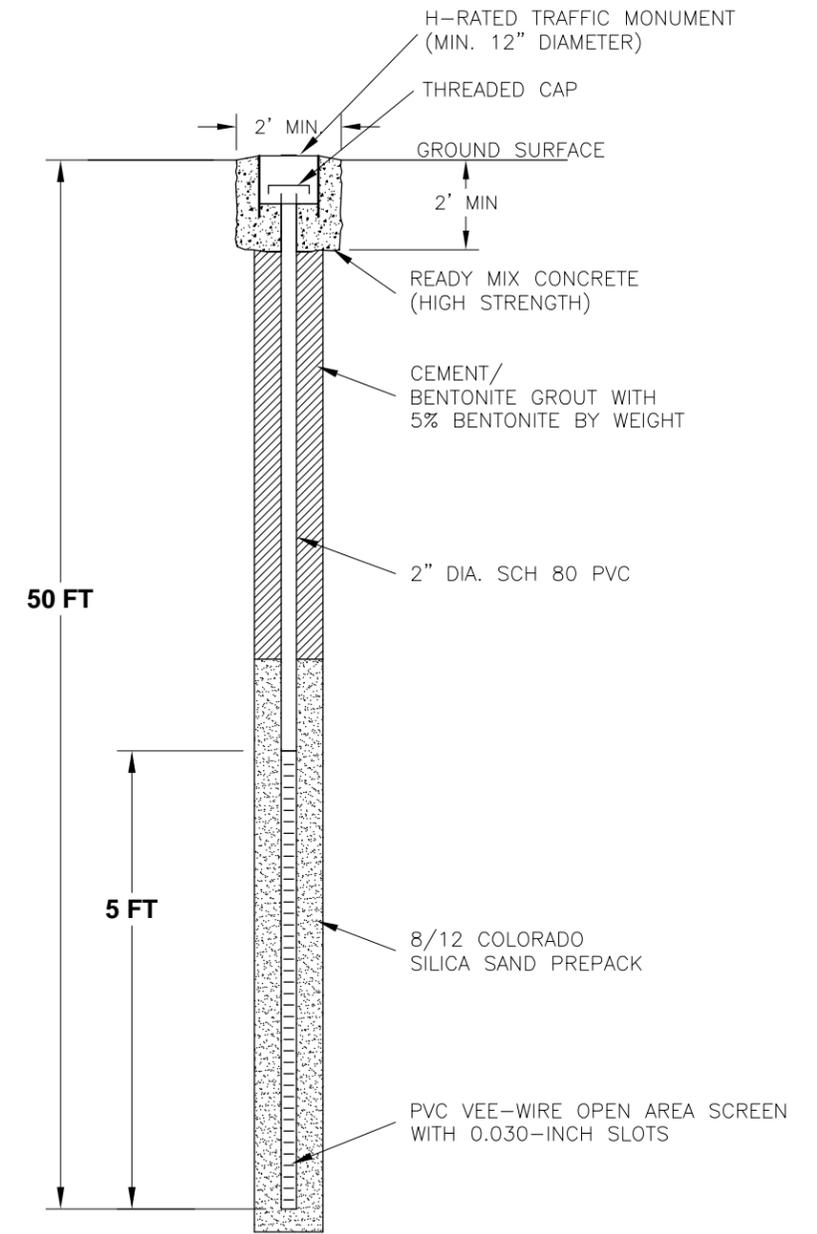


<p>CO₂ PILOT STUDY CROSS SECTION C-C' Former Rhone-Poulenc Site Tukwila, Washington</p>		
By: APS	Date: 09/15/16	Project No. 8769.005
<p>Amec Foster Wheeler Environment & Infrastructure, Inc.</p>		<p>Figure 7</p>

Plot Date: 09/15/16 - 3:19pm. Plotted by: adam.stenberg
 Drawing Path: C:\Users\adam.stenberg\appdata\local\temp\AcPublish_5560\ Drawing Name: FRP_SiteMap-pH-PilotStudy-CrossSect_090216.dwg



1 OBSERVATION / VENT WELL DETAIL
NOT TO SCALE



2 INJECTION WELL DETAIL
NOT TO SCALE

PILOT STUDY NEW OBSERVATION WELLS APPROXIMATE WELL DIMENSIONS (FT)			
WELL ID	A	B	CASING
IMW A1-D	50	5	2" DIA SCH 80 PVC
IMW B1-S	35	10	2" DIA SCH 80 PVC
IMW B1-D	50	5	2" DIA SCH 80 PVC
IMW C1-S	27.5	10	2" DIA SCH 80 PVC
IMW A2-S	35	10	2" DIA SCH 80 PVC
IMW A2-D	50	5	2" DIA SCH 80 PVC
IMW B2-S	27.5	10	2" DIA SCH 80 PVC
VENT WELL	25	15	2" DIA SCH 40 PVC

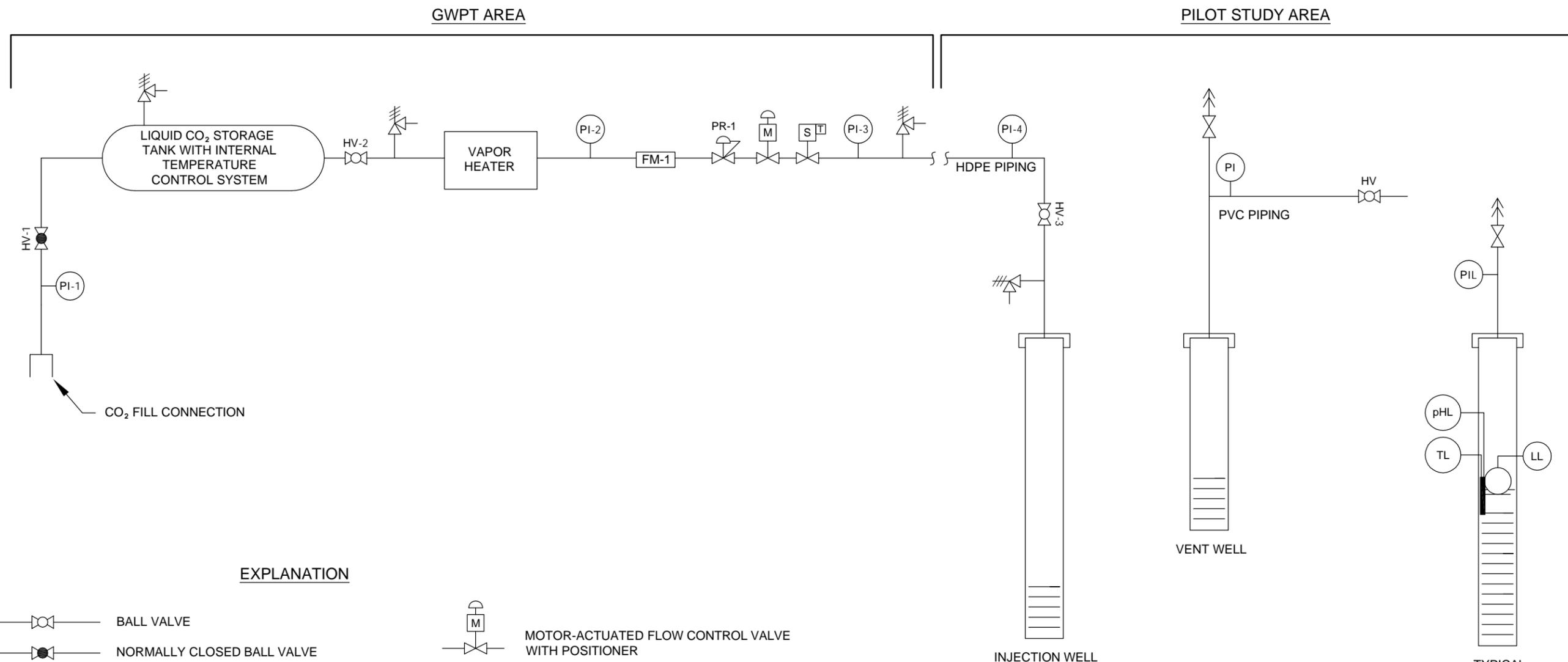
NOTES:

1. WELL DEPTHS AND SCREEN INTERVALS ARE APPROXIMATE. FINAL DEPTH WILL BE DETERMINED BASED ON FIELD OBSERVATIONS.
2. THE DEPTH OF INJECTION WELL SAND PACK ABOVE THE SCREEN WILL BE DETERMINED IN THE FIELD BASED ON THE OBSERVED LOCATION OF THE SILTY SAND ZONE.



PROPOSED PILOT STUDY WELL DETAILS Former Rhone-Poulenc Site Tukwila, Washington		
By: APS	Date: 11/21/16	Project No. 08769
Amec Foster Wheeler Environment & Infrastructure, Inc.		DRAWING 1

Plot Date: 09/12/16 - 1:13pm, Plotted by: adam.stenberg
 Drawing Path: S:\8769_2006\112_CMS Work Plan\CAD\ Drawing Name: FRP_SiteMap-pH-PilotStudy-Fig5-ZOOM_090216.dwg



EXPLANATION

- | | | | |
|------|--------------------------------------------------|--|---------------------------------------------------|
| | BALL VALVE | | MOTOR-ACTUATED FLOW CONTROL VALVE WITH POSITIONER |
| | NORMALLY CLOSED BALL VALVE | | LEVEL LOGGING TRANSDUCER |
| | SAMPLE PORT | | PRESSURE INDICATOR |
| | PRESSURE RELIEF VALVE | | PRESSURE INDICATING LOGGER |
| | REGULATED SIDE PRESSURE REGULATING CONTROL VALVE | | pH LOGGER |
| | TIMER ACTUATED SOLENOID VALVE | | TEMPERATURE LOGGER |
| | QUICK CONNECT CAM-LOCK FITTING | | |
| | THREADED OR GLUED CAP | | |
| | FLOW METER | | |
| HV = | HAND VALVE | | |
| PR = | PRESSURE REGULATOR | | |

NOTE:

1. WELL DEPTHS AND SCREEN INTERVALS ARE APPROXIMATE. FINAL DEPTH WILL BE DETERMINED BASED ON FIELD OBSERVATIONS.
2. OBSERVATION WELL pH AND TEMPERATURE READINGS MAY BE MANUAL MEASUREMENTS.



CO₂ INJECTION SYSTEM PROCESS AND INSTRUMENTATION DIAGRAM Former Rhone-Poulenc Site Tukwila, Washington		
By: APS	Date: 09/12/16	Project No. 08769
Amec Foster Wheeler Environment & Infrastructure, Inc.		P&ID 01



ATTACHMENT A

Calculations for CO₂ Injection Pressures

DESIGN MEMORANDUM

Client: Container Properties

Sheet 1 Of 1

Project: FRP CMS WP

Date: 12/16/2015

Data For: CO₂ Pilot Study WP

Work Order: _____

Prepared By: CDH Checked By: LMM

File No: _____



Note: This form must be used for project calculations and original filed in project files

Purpose:

To determine range of injection pressures for the CO₂ Pilot Study Work Plan (PSWP).

From the guidance document "In-Situ Air Sparging: Engineer Manual" by the US Army Core of Engineers (USACE) published 31 December 2013 (USACE, 2013); The maximum injection pressure or overburden pressure to prevent fracture formation in the aquifer is:

$$\text{Overburden pressure} = P_{ob} = \text{Pressure soil column} + \text{Pressure water column} = P_{sc} + P_{wc}$$

$$\text{where } P_{wc} = (\text{depth}_{\text{top well screen}} - \text{depth}_{\text{to water table}}) (\text{s.g. water}) (\phi) (9.8 \text{ kN/m}^3)$$

$$\text{and } P_{sc} = (\text{depth}_{\text{top well screen}}) (\text{s.g. soil}) (1 - \phi) (9.8 \text{ kN/m}^3)$$

Assumptions:

$$\text{Soil SG} = \text{s.g. soil} = 2.5 ; \text{ Porosity} = \phi = 0.5 \text{ (conservative estimate)}$$

$$\text{Water SG} = \text{s.g. water} = 1.0 ; \text{ depth}_{\text{top well screen}} = d_{tws} = 50 \text{ ft for MW-54 ; } \text{depth}_{\text{to water table}} = d_{wt} = 15 \text{ ft}$$

$$P_{wc} = (d_{tws} - d_{wt}) (\text{s.g. water}) (\phi) (9.8 \text{ kPa}) = (35 \text{ ft}) (1.0) (0.5) (9.8 \text{ kPa}) = 52.3 \text{ kPa} = \underline{7.6 \text{ psig}}$$

$$P_{sc} = (d_{tws}) (\text{s.g. soil}) (1 - \phi) (9.8 \text{ kPa}) = (50 \text{ ft}) (0.3048 \text{ m/ft}) (2.5) (0.5) (9.8 \text{ kPa}) = 184.8 \text{ kPa} = \underline{26.8 \text{ psig}}$$

$$P_{ob} = P_{sc} + P_{wc} = 26.8 \text{ psig} + 7.6 \text{ psig} = 34.4 \text{ psig}$$

In accordance with (USACE, 2013), max injection pressure = $P_{ob} \times \text{Safety factor (20-40\%)} = P_{max}$ for a 20% SF:

$$* P_{max} = P_{ob} \times 0.8 = 34.4 \text{ psig} \times 0.8 = 27.5 \text{ psig} \approx \boxed{28 \text{ psig}}$$

From (USACE, 2013), the minimum injection pressure (P_{min}) is the pressure required to overcome the hydrostatic pressure (P_h) and the aquifer formation entry pressure (P_{ent}), or:

$$P_{min} = P_h + P_{ent} = (d_{tws} - d_{wt}) (P_w \times g) + P_{ent}$$

Assumptions:

$$d_{tws} = 50 \text{ ft} ; d_{wt} = 15 \text{ ft} ; (P_w) (g) = 0.43 \text{ psi/ft H}_2\text{O}$$

$P_{ent} = 0.44 \text{ psig}$ for fine to med sand and 4.4 psig for a silt (USACE, 2013); taking the avg for a silty sand: $(0.44 \text{ psig} + 4.4 \text{ psig}) / 2 = 2.4 \text{ psig}$

$$* P_{min} = (35 \text{ ft}) (0.43 \text{ psi/ft H}_2\text{O}) + 2.4 \text{ psig} = 17.45 \text{ psig} \approx \boxed{17 \text{ psig}}$$