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January 22, 2010

Aaron Yue California Department of Toxic Substances Control 5796 Corporate Avenue Cypress, CA 90630

Pamela Innis U.S. Department of the Interior, Office of Environmental Policy and Compliance P.O. Box 25007 (D-108) Denver Federal Center, Bldg. 56 Denver, CO 80225-0007

Subject:Submittal of Technical Memorandum: Methods of Estimating Pore
Volume Flushing Efficiency Used in Calculating Mass Removal Rates for
CMS/FS Alternatives, PG&E Topock Compressor Station, Needles,
California

Dear Mr. Yue and Ms. Innis:

This letter transmits the technical memorandum: *Methods of Estimating Pore Volume Flushing Efficiency Used in Calculating Mass Removal Rates for CMS/FS Alternatives*, at the PG&E Topock Compressor Station. This technical memorandum has been prepared in conformance with the resolution to comment #399 in the Final Corrective Measures Study/Feasibility Study Report, dated December 16, 2009.

Please do not hesitate to contact me at (805) 234-2257 with any questions or comments on the attached technical memorandum.

Sincerely,

Geonne Macks

Yvonne Meeks Topock Project Manager

Methods of Estimating Pore Volume Flushing Efficiency Used in Calculating Mass Removal Rates for CMS/FS Alternatives, PG&E Topock Compressor Station, Needles, California

Date: January 22, 2010

Executive Summary

Four sets of data were used to estimate the number of pore volume flushes required to replace 95 percent of groundwater from the aquifer matrix. The estimates ranged between 1.5 and 10.1 pore volumes, with the majority of estimates being less than 5.0 pore volumes. These estimates were used in the *Groundwater Corrective Measures Study/Feasibility Study Report for SWMU 1/AOC 1 and AOC 10, PG&E Topock Compressor Station, Needles, California* (CMS/FS Report) (CH2M HILL, 2009a) for the purpose of comparing alternatives. In the CMS/FS Report, the time for 98 percent mass removal was calculated for each alternative assuming that 2.0, 5.0, and 20.0 pore volumes were required. This technical memorandum documents the background information for the pore volume assumptions in the CMS/FS Report.

Introduction

This memorandum provides a description of the concepts and methods used in the CMS/FS Report for Solid Waste Management Unit (SWMU) 1/Area of Concern (AOC) 1 and AOC 10 at the Pacific Gas and Electric Company (PG&E) Topock Compressor Station to estimate the number of mobile pore volume flushes required to reduce the concentration of hexavalent chromium [Cr(VI)] to target levels. This memorandum has been prepared in response to comments on the CMS/FS Report (CH2M HILL, 2009a) requesting explanation and technical backup for the five mobile-pore-volume-flushing estimate and the 2.0 to 20.0 mobile-pore-volume range used in simulating mass removal time for alternatives in the CMS/FS Report (see United States Department of the Interior response to comment #399 in Appendix C of the CMS/FS Report; CH2M HILL, 2009a).

Flushing efficiency is a measure of how many mobile pore volumes of clean water need to be flushed through the aquifer to reduce contaminant concentrations to a target level. To develop estimates of flushing efficiency for the Topock site, several sets of monitoring well data with natural and introduced tracer concentrations were used to estimate the mobilepore-volume-flushing requirements for a given amount of concentration change.

Four separate groundwater data sets were analyzed:

• Natural Tracers: Stable Isotopes in the Floodplain

- Breakthrough of Injected water from IW-2 in the Upland
- In-situ Pilot Test Tracers in the Floodplain
- In-situ Pilot Test Tracers in the Upland

The data and methods are described in detail below.

Natural Tracers: Stable Isotopes

Floodplain wells have been monitored for the stable isotopes deuterium (²H) and oxygen-18 (¹⁸O) since early 2004, when the first stages of interim measures (IM) extraction were being implemented. The isotopic signatures of groundwater and surface water were produced by comparing ²H and ¹⁸O to standards, resulting in "delta" values δ²H and δ¹⁸O, measured in parts per thousand (ppt) difference from a standard. As discussed in the *RCRA Facility Investigation/Remedial Investigation Report, PG&E Topock Compressor Station, Needles, California: Volume 2 – Hydrogeologic Characterization and Results of Groundwater and Surface Water Investigation* (RFI/RI Volume 2 Report) (CH2M HILL, 2009b), river water and shallow fluvial groundwater close to the river have a very light isotopic signature, with δ²H values ranging from -104 to -83 ppt. By contrast, high-Cr(VI) plume samples have δ²H values in the -68 to -37 ppt range. This strong contrast between isotopic end members provides a natural tracer tool with which to measure pore flushing resulting from IM groundwater extraction over time.

Several floodplain wells have shown significant changes in isotopic signature as IM extraction has increased and continued since 2004. The effect of the extraction is to maintain a landward groundwater gradient that draws river water and shallow fluvial groundwater (collectively referred to herein as "river-signature water") westward and downward through the floodplain aquifer toward the pumping wells. The monitoring wells in between the river and the pumping wells showed effects of this process by becoming more "river-like" in their isotopic signature. The groundwater model was used with IM pumping history to calculate the number of pore volumes of river-signature water that passed through each well over time. The pumping rates and wells have changed over time and, for simplicity, the IM extraction was broken down into three periods with the following average pumping rates:

- **Phase 1:** March to October 2004: MW-20 cluster (4.0 gallons per minute [gpm]) and TW-2D (17.1 gpm)
- Phase 2: October 2004 to February 2006: TW-2D (77.3 gpm)
- Phase 3: February 2006 to present: TW-3D (97.3 gpm) and PE-1 (34.2 gpm)

The floodplain wells from the MW-30, MW-34, and MW-39 clusters that showed a progressively stronger river signature during this time are listed in Table 1 and shown in Figure 1. (All tables and figures are provided at the end of this technical memorandum.) The following methods were used to estimate mobile pore volume flushes for each of these wells:

- 1. **Mark the location of the nearest river-signature water to the monitoring wells in the model.** Based on monitoring well and river data that have defined river-signature water and the site conceptual model described in the RFI/RI Volume 2 Report, the estimated western edge of the shallow zone river-signature groundwater was identified. Nodes in the groundwater model corresponding to this river-water boundary were "marked." By the same methods, the western edges of the middle and deep zone river-signature groundwater were also marked in the model. The marked areas are shown in Figure 1 and are based on the distribution of reducing, fluvial groundwater that has a river isotopic signature. These marked zones represent the closest river-signature groundwater to the floodplain wells that have exhibited changes in isotopic signature toward a river signature.
- 2. Estimate the time for one mobile pore volume of river-signature water to travel to each monitoring well. The shortest simulated time of travel from any of the marked zones to the well being examined represents one mobile pore volume flushed by river-signature water. Steady-state model runs were made using pumping distributions for each of the three pumping phases listed above, and the shortest travel time to each well was recorded for each phase. A listing of the simulated mobile pore volume flushing times is provided in Table 2.
- 3. Develop flushing model and expressions for changing δ^2 H values over time. Flushing of the wells with river-signature water was modeled as the classic exponential decay curve, of the form $C/C_0 = e^{-kt}$, where C represents concentration at time t, C_0 is the starting concentration (t=0), and k is the decay constant. For the purposes of this study, t was defined in terms of mobile-pore-volume-flushing times. The assigned starting concentration was the last measurement during Phase 1 since there was no flushing of river water to the target wells during that period. At zero pore volumes flushed (or t=0), $C/C_0 = 1$. As time progressed and the isotopic signature became lighter or more river-like, the C/C_0 ratio grew lower and lower. The boundary condition for the equation is when the well sample represents 100 percent riversignature water and $C/C_0 = 0$, meaning none of the original groundwater is present in the aquifer at the well. Given these relationships, the C/C_0 for each data point was calculated as $(\delta^2 H_t - \delta^2 H_r)/(\delta^2 H_0 - \delta^2 H_r)$, where $\delta^2 H_t$ is the $\delta^2 H$ value at the sample collection date, $\delta^2 H_r$ is the $\delta^2 H$ value assigned to river-signature water, and $\delta^2 H_0$ is the δ^2 H value on the initial sample collection date for that well. The δ^2 H value assigned to represent $\delta^2 H_r$ was -100.3 ppt; this represents an end-member signature defined as the mean of all measured river-signature δ^2 H values through September 2009 minus one standard deviation. The standard deviation was subtracted to provide a light (i.e., more negative) end member that is unmistakably a river signature.
- 4. Estimate the number of mobile pore volumes that have flushed through aquifer near the well for each sample date. The number of mobile pore volumes that had flushed through the aquifer at each well since the first sample collection date was calculated for each subsequent sampling date. This was done by determining the pumping phase into which the collection date fell and dividing the amount of time that had passed in that phase by the pore volume flushing time for the well in that phase, as calculated in Bullet 2 above. The result was then added to the cumulative pore volume total for previous sample collection dates.

- 5. Plot C/C_0 vs. pore volumes for each monitoring well and fit model curve. For each sampling date, the C/C_0 calculated in Bullet 3 above was plotted against the pore volumes flushed calculated in Bullet 4. A best-fit exponential curve was fitted to the data, and the decay constant k was recorded for each well. These are listed in Table 2, and the plots and curves are shown in Figures 2a and 2b.
- 6. Estimate pore volume flushing requirement for each well. Finally, the number of pore volume flushes needed to achieve 95 percent river-signature water (i.e., $C/C_0 = 0.05$) was calculated using the decay curve equations. The 95 percent level was used due to the lack of defining data between 95 percent and 100 percent river-signature water and the fact that the exponential curve tends to infinity as C/C_0 approaches zero.

As listed in Table 2 and shown in Figures 2a and 2b, the pore-volume-flushing estimates range between 2.0 and 10.1 pore volumes. The range is expected given the numerous uncertainties associated with the flushing model. This was the basis of the 2.0 to 20.0 pore volume range used in the CMS/FS Report (CH2M HILL, 2009a). Well MW-30-50 and the wells from the MW-34 cluster had more data points than the MW-39 wells and therefore are considered stronger estimates. The main uncertainties are as follows:

- Natural variability in δ²H values of groundwater and river water. This is demonstrated by the river-signature water (assumed constant in the flushing model), which has ranged from -103.6 to -83.0 over the study period. Some of this variation may be attributed to laboratory analytical uncertainty, but that is relatively low (laboratory precision is reported to be 0.16 ppt).
- Uncertainty associated with the modeled time of river-signature water to arrive at the floodplain well clusters. This includes uncertainty in hydraulic parameter estimates, the assumed location of river-signature water, and the use of average pumping rates of IM extraction wells.
- Variability in parameters such as mobile and immobile porosity, dispersion, retardation factors, etc. These parameters are not easily measured but are assumed to be implicit in the flushing model. Natural variation in these parameters would also contribute to uncertainty in the flushing model.

Breakthrough of Injected Water from IW-2

During the startup at injection well IW-2, water quality was monitored in several observation wells surrounding the injection well. The changes in total dissolved solids (TDS) from three observation wells (OW-1D, OW-2D, and OW-5D) showed the breakthrough of injected water as indicated by a reduction in TDS. The lower TDS in the injected water displaced the higher TDS that resided in the aquifer prior to injection. Using an assumption of uniform radial flow outward from the injection well, data from these wells were used to estimate the transport porosity and dispersivity of the aquifer. However, these data can also be used to estimate the number of mobile pore volumes it took for the TDS level in the monitoring wells to change to 95 percent of the difference between the initial TDS and the final injection-water TDS. Table 3 shows the computation of how many mobile pore volumes of injected water it took to achieve a concentration change equal to 95 percent

of the original concentration difference between the original groundwater quality and the steady concentration after injection. The groundwater model was not used in this estimation. The distance from IW-2 for each monitoring well was used to compute a pore volume of injection water. The volume consists of the radial distance from the injection well, the thickness of the deep aquifer zone (where the majority of injected flow occurs), and the transport velocity computed for each well. This computed volume of the cylinder of aquifer material extending radially from the injection well to the monitoring well was divided by the average injection rate to calculate the pore volume flushing time. The time at which 95 percent of the starting TDS concentration had been replaced by the TDS of the injected water was then directly converted to the number of pore volumes that have flushed through the system. As shown in Table 3, the number of calculated pore volumes required to reach the 95 percent endpoint ranged from 1.5 to 2.2, corresponding to the low end of the range computed with stable isotope data.

In-situ Pilot Testing Tracers: Floodplain

During floodplain in-situ pilot testing, several tracers were introduced into the injection wells PTI-1S, -1M, and -1D. Observed tracer concentration data at well PT-2D showed the injected tracers arrive at the well and then slowly decay as each tracer was flushed out of the aquifer. The tracer concentration decay data were used to estimate the number of pore volumes required to flush the tracer out of the aquifer in the screened interval using a dual-domain analytical model and an empirical model. The approach is described in detail in Attachment A. The calculated number of pore volumes to achieve 95 percent reduction in tracer concentration was 2.0 in the dual domain analytical model , and this was supported by a calculated range of 1.5 to 4.5 pore volumes in the empirical model.

In-situ Pilot Testing Tracers: Uplands Area

Tracer data from the uplands in-situ pilot testing program were also used to make estimates of pore volume flushing efficiency in a method using a groundwater model of the uplands pilot test area, as described in Attachment B. This approach resulted in an estimate of approximately three pore volumes to achieve 95 percent reduction in tracer concentration.

Conclusions

Four sets of data were used to estimate the number of pore volume flushes required to replace 95 percent of groundwater from the aquifer matrix. The estimates ranged between 1.5 and 10.1 pore volumes, with the majority of estimates being less than 5.0 pore volumes. These estimates were applied to the CMS/FS Report (CH2M HILL, 2009a) for the purpose of comparing alternatives. In that study, the time for 98 percent mass removal was calculated for each alternative assuming 2.0, 5.0, and 20.0 pore volumes were required.

References

CH2M HILL. 2009a. *Groundwater Corrective Measures Study/Feasibility Study Report for SWMU* 1/AOC 1 and AOC 10, PG&E Topock Compressor Station, Needles, California. Report submitted to DTSC. December.

. 2009b. RCRA Facility Investigation/Remedial Investigation Report, PG&E Topock Compressor Station, Needles, California: Volume 2 – Hydrogeologic Characterization and Results of Groundwater and Surface Water Investigation. Report submitted to DTSC. February 11.

Tables

- 1 Stable Isotope and Chromium Data for Samples Used in Pore Water Flushing Model
- 2 Stable Isotope Flushing Model Summary
- 3 Parameters and Estimates Produced Using Specific Conductance Data near IM No. 3 Injection Wells

Figures

- 1 Location of Wells and River-Signature Zones Used in the Pore Volume Flushing Model
- 2a Change in Stable Isotope Signature vs. Modeled Pore Volume Flushing
- 2b Change in Stable Isotope Signature vs. Modeled Pore Volume Flushing

Attachments

- A Analysis of Tracer Data from the Floodplain In-situ Pilot Tests
- B Analysis with Uplands In-situ Pilot Test Numerical Flow and Transport Model

Tables

TABLE 1

Stable Isotope and Chromium Data for Samples Used in Pore Water Flushing Model Pore Volume Flushing Estimate Methods PG&E Topock Compressor Station, Needles, California

Floodnlain wells showing	isotonic si	nature change
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River-signature water samples.

Well	Sample Date	Cr(VI)	δ ¹⁸ Ο	δ²Η
MW-30-050	03/05/04	83	-6.4	-58
	05/14/04	2,010	-7.7	-54
	09/23/04	831	-7.3	-58
	12/15/04	29	-7.9	-63
	03/10/05	ND	-8.3	-68
	10/07/05	ND	-9.4	-79
	12/16/05	ND	-10.5	-65
	03/09/06	ND	-9.8	-83.5
	05/02/06	ND	-10.4	-73.6
	10/11/06	ND	-10.7	-82.2
MW-34-055	03/04/04	ND	-9.6	-77
	05/13/04	ND	-10.3	-77
	09/22/04	ND	-11	-82
	12/15/04	ND	-10.9	-83
	03/10/05	ND	-10.8	-82
	07/15/05	ND	-10.3	-84
	10/05/05	ND	-10.6	-88
	12/14/05	ND	-10.8	-74
	03/08/06	ND	-10.8	-86.8
	05/03/06	ND	-11.5	-84.3
	10/04/06	ND	-12.2	-94.8
	10/03/07	ND	-11.3	-96.6
	10/07/08	ND	-13	-100

Sample ID	Sample Type	Sample Date	Cr(VI)	δ ¹⁸ Ο	δ²H
I-3	River	06/10/04	ND	-12.1	-98
MW-27-020	Well	03/03/04	ND	-11.7	-100
		05/12/04	ND	-11.3	-98
		09/21/04	ND	-12.3	-92
		12/15/04	ND	-11.9	-101
		03/08/05	ND	-12	-102
		07/18/05	ND	-11.9	-98
		10/05/05	ND	-11.8	-102
		12/14/05	ND	-11.7	-91
		03/06/06	ND	-12.1	-90.9
		06/14/06	ND	-12	-89.8
		10/03/06	ND	-13.1	-96.6
		10/02/07	ND	-12.5	-96.3
MW-28-025	Well	03/04/04	ND	-11.3	-95
		05/11/04	ND	-11.3	-95
		06/07/04	ND	-12.5	-100
		09/20/04	ND	-11.7	-89
		12/14/04	ND	-12	-99
		03/10/05	ND	-12.2	-95
		06/15/05	ND	-11.6	-91
		10/06/05	ND	-11.7	-95
		12/16/05	ND	-11.4	-90
		03/09/06	ND	-11.5	-93.9

Average

Std Dev

-12.0

0.5

-95.9

4.4

TABLES

TABLE 1

Stable Isotope and Chromium Data for Samples Used in Pore Water Flushing Model Pore Volume Flushing Estimate Methods PG&E Topock Compressor Station, Needles, California

Average	-12.0	-95.9
Std Dev	0.5	4.4

Floodplain wells showing isotopic signature change.

River-signature water samples.

Well	Sample Date	Cr(VI)	δ ¹⁸ Ο	δ²Η
MW-34-055	09/30/09	ND	-10.85	-100.79
MW-34-080	03/05/04	26	-8.9	-75
	05/13/04	ND	-10.2	-77
	09/23/04	ND	-9.9	-79
	03/08/05	ND	-10.4	-83
	06/30/05	ND	-8.4	-82
	10/05/05	ND	-10.1	-85
	12/14/05	ND	-10.2	-71
	03/09/06	ND	-9.9	-86.8
	05/03/06	ND	-11.7	-77.6
	10/04/06	ND	-11.3	-81.8
	12/12/06	ND	-10.5	-80.9
	03/05/07	ND	-11.5	-85.8
	04/30/07	ND	-11.5	-88.9
	10/03/07	ND	-11.3	-87.8
	03/12/08	ND	-11.4	-87.3
	05/06/08	ND	-11.4	-87.3
	10/07/08	ND	-11.8	-87.6
	12/10/08	ND	-10.97	-93.1
	03/10/09	ND	-10.85	-84.77
	04/30/09	ND	-11.45	-85.79
	09/30/09	ND	-9.6	-88.93

Sample ID	Sample Type	Sample Date	Cr(VI)	δ ¹⁸ Ο	$\delta^2 H$
MW-28-025	Well	05/05/06	ND	-11.4	-90.3
		10/11/06	ND	-12.2	-95
		10/04/07	ND	-12.1	-98.7
NR-1	River	06/11/04	ND	-11.8	-95
R-27	River	03/03/04	ND	-11.4	-86
		05/12/04	ND	-11.4	-96
		09/22/04	ND	-12.1	-98
		12/13/04	ND	-11.4	-95
		03/07/05	ND	-12.3	-102
		06/14/05	ND	-11.4	-92
		10/05/05	ND	-11.6	-94
		12/16/05	ND	-11.7	-87
		03/06/06	ND	-11.8	-92.1
		05/03/06	ND	-12.8	-93.9
		10/04/06	ND	-12.2	-94.9
		12/20/06	ND	-12.7	-98.1
		03/13/07	ND	-13	-99.5
		05/08/07	ND	-12.9	-103.6
		12/05/07	ND	-11.7	-99
		06/17/08	ND	-13	-101.4
R-28	River	03/03/04	ND	-11.3	-90
		05/12/04	ND	-11.5	-98

TABLES

TABLE 1

Stable Isotope and Chromium Data for Samples Used in Pore Water Flushing Model

Pore Volume Flushing Estimate Methods

PG&E Topock Compressor Station, Needles, California

Average	-12.0	-95.9
Std Dev	0.5	4.4

Floodplain wells showing isotopic signature change.

River-signature water samples.

Well	Sample Date	Cr(VI)	δ ¹⁸ Ο	$\delta^2 H$
MW-34-100	06/21/05	560	-9.7	-75
	10/05/05	732	-9.9	-83
	03/08/06	800	-11.4	-75.5
	05/03/06	900	-10.5	-74.5
	04/30/07	626	-10.9	-80.7
	10/03/07	521	-10.2	-78.2
	10/07/08	286	-11	-81.3
MW-39-040	06/18/04	ND	-5.5	-45
	06/16/05	ND	-6.8	-50
	03/07/06	ND	-7.5	-60.4
MW-39-060	06/18/04	3,540	-4.6	-42
	03/08/06	7.1	-9.7	-67.9
	05/02/06	1.1	-9.7	-72.9
MW-39-070	06/18/04	8,210	-5	-44
	06/16/05	799	-8.7	-64
	03/08/06	200	-9.5	-66.9

Sample ID	Sample Type	Sample Date	Cr(VI)	δ ¹⁸ Ο	$\delta^2 H$
R-28	River	09/22/04	ND	-12.1	-99
		12/13/04	ND	-11.1	-95
		03/08/05	ND	-12.5	-102
		06/14/05	ND	-11.6	-95
		10/05/05	ND	-11.6	-94
		12/16/05	ND	-11.5	-83
		03/06/06	ND	-12.3	-93.4
		05/03/06	ND	-13	-92.1
		10/04/06	ND	-12.6	-95.3
		12/20/06	ND	-12.4	-99.6
		03/14/07	ND	-12.8	-100.4
		05/09/07	ND	-13	-102.3
		12/06/07	ND	-11.7	-98.6
		06/18/08	ND	-13.2	-101.7
		12/04/08	ND	-11.89	-97
		01/21/09	ND	-11.97	-96.7
		04/09/09	ND	-12.43	-97.81
		07/08/09	ND	-12.78	-98.62
		09/09/09	ND	-12.47	-99.06

Notes:

Cr(VI) in $\mu g/L.$ $\delta^{18}O$ and δ^2H in parts per thousand difference from standard.

TABLE 2 Stable Isotope Flushing Model Summary Pore Volume Flushing Estimate Methods PG&E Topock Compressor Station, Needles, California

	Modeled tim under cond	e for one pore v itions of each p	volume flush hase (days)	Total modeled pore volumes of river- signature water passing through well over duration of each phase			Calculated decay constant	Calculated number of pore volumes to reach 95% river- signature water content
Well	Phase 1 ^a	Phase 2	Phase 3	Phase 1 ^a	Phase 2	Phase 3 ^b		
MW-30-050	NA	690	309	NA	0.71	4.33	0.646	4.6
MW-34-055	NA	183	66	NA	2.67	20.26	0.296	10.1
MW-34-080	NA	2061	708	NA	0.24	1.89	0.343	8.7
MW-34-100	NA	14064	4728	NA	0.03	0.28	1.358	2.2
MW-39-040	NA	861	486	NA	0.57	2.75	0.477	6.3
MW-39-060	NA	1512	477	NA	0.32	2.80	1.479	2.0
MW-39-070	NA	981	450	NA	0.50	2.97	1.04	2.9

General Notes:

Phase 1 = 3/1/04 to 10/1/04. Phase 2 = 10/1/04 to 2/1/06. Phase 3 = 2/1/06 to present.

Specific Notes:

^a Model does not predict transport of river-signature water to floodplain wells under the conditions of Phase 1. ^b For purposes of calculation, assume Phase 3 ends at the time of the most recent sample, 9/30/09.

TABLE 3Parameters and Estimates Produced Using Specific Conductance Data Near IM3 Injection WellsPore Volume Flushing Estimate MethodsPG&E Topock Compressor Station, Needles, California

Well	Distance from Injection Well (ft)	Transport Porosity	Lower Aquifer Thickness	Mobile Pore Volume to Monitoring Well (ft ³)	Injection Rate (mobile pore volumes per day)	Time to Reach 95% of Initial Concentration Difference (d)	Mobile Pore Volumes to Reach 95% of Injected Water Concentration
OW-1D	93	0.13	50	176,526	0.01526	95.1	1.5
OW-2D	38	0.14	65	41,260	0.224	10	2.2
OW-5D	207	0.11	65	962,003	0.1234	148.7	1.8

Figures



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MW-34-55

MW-34-100

FIGURE 2a Change in Stable Isotope Signature vs. Modeled Pore Volme Flushing Pore Volume Flushing Estimate Methods PG&E Topock Compressor Station

CH2MHILL









Pore Volumes

FIGURE 2b Change in Stable Isotope Signature vs. Modeled Pore Volme Flushing Pore Volume Flushing Estimate Methods PG&E Topock Compressor Station



Attachment A Analysis of Tracer Data from the Floodplain In-situ Pilot Tests



ARCADIS 630 Plaza Drive Suite 200 Highlands Ranch Colorado 80129 Tel 720.344.3500 Fax 720.344.3535

TECHNICAL MEMORANDUM

Date: January 22, 2010 ARCADIS Project No.: RC000689.0001

Subject:

Technical Basis for Pore Volume Flushes for CMS Alternatives Modeling, Pacific Gas and Electric (PG&E) Compressor Station, Topock, California.

ATTACHMENT A - Analysis of Tracer Data from the Floodplain In Situ Pilot Tests

Introduction

The purpose of this technical memorandum is to develop a technical basis for the number of pore volumes needed to attain cleanup goals by interpretation of tracer breakthrough data from the floodplain pilot tests.

Approach

For this analysis, breakthrough data resulting from tracer injection at floodplain site are used. Both a physically-based analytical model and an empirical model are used to analyze the tracer data.

Summary of Floodplain Pilot Tests and Tracer Data

Pacific Gas and Electric (PG&E) implemented a floodplain reductive zone in-situ pilot test (ISPT) to address chromium concentrations in groundwater at the Topock Compressor Station near Needles, California (Figure A1). The groundwater in the pilot test area is present in unconsolidated alluvial and fluvial deposits, referred to collectively as the alluvial aquifer. The thickness of the alluvial aquifer ranges from 30 to 180 feet. Thickness increases from south to north. The aquifer at the ISPT is divided into three hydrostratigraphic units, shallow [35 to 45 feet below ground surface {bgs}], middle (60 to 70 feet bgs], and deep (95 to 105 feet bgs). As part of the interim measure number 3 (IM-3), extraction wells were installed in the floodplain area. General groundwater flow direction at the ISPT is towards extraction wells TW-2D and TW-3D (Figure A1); this is the result of continued high extraction rates for the IM-3 system. Water-level measurements obtained with pressure transducers placed in monitoring wells provide a quantitative description of hydraulic gradients and flow paths which was presented in the Topock Floodplain Report (ARCADIS 2008). The hydrogeologic parameters - including hydraulic conductivity, hydraulic gradient, and porosity - thus obtained are used for this flushing analysis as initial values.

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The floodplain ISPT consisted of injecting a reagent mixture into well cluster PTI-1 S/M/D and monitoring the results in six three-level well nests (PT-1 through PT-6). Figure A1 provides location of these monitoring and injection wells.

Six injections occurred for the floodplain ISPT from May 2006 through July 2007. The first injection event was completed in the injection well cluster (PTI-1S, PTI-1M and PTI-1D) and injection events two through six were completed in injection well PTI-1D only. The pilot tests were performed by injecting tracer and carbon substrate into the aquifer for relatively short time periods. Aquifer response was observed by sampling monitoring wells during the injection event and then during post-injection periods to monitor drift toward the extraction well. Because the most complete set of injections and monitoring data were obtained for the deep zone, these data are used in the tracer flushing analysis. The summaries of injection tests for the deep zone are given in Table A1. The PT-1 and PT-3 well clusters are dose monitoring wells and are located within the radius of influence (ROI) that developed during injections. Well clusters PT-4, PT-5 and PT-6 are up-gradient wells (Figure A1). Well cluster PT-2D is located downgradient of the injection ROI and therefore, is used in the tracer flushing analysis presented in this letter report. The well PT-2D is at a distance of 44.7 feet from the PTI-1 injection well.

Physically-Based Conceptual Model of Tracer Flushing

Tracer migration through the aquifer at the ISPT is conceptualized as resulting from dual-domain solute transport. In dual-domain porous media, the pore structure is modeled as two overlapping continua, one with groundwater that flows through well interconnected "mobile" pores and a second with groundwater that is relatively immobile. Tracer migrates primarily through the mobile pore spaces by advection with mass transfer between mobile and immobile pore spaces occurring by diffusion. Mathematically, this process is represented by dividing the porosity into separate mobile and immobile porosity domains with mass transfer between the two pore spaces controlled by diffusion (described by a first order mass transfer rate coefficient).

The tracer moves through mobile pore spaces by advection at the mobile pore-water velocity. In the absence of dual-domain mass transfer, the travel time to a downgradient location would coincide with the time of breakthrough for $C/C_o = 0.5$ where C is tracer concentration observed at the downgradient location and C_o is the initial concentration within the injection ROI. However, dual domain mass transfer slows the apparent rate of tracer migration. As distance from the point of injection increases, the time for breakthrough corresponding to the mobile pore-water velocity occurs before the time for $C/C_o = 0.5$. Similarly as distance from the point of injection increases at larger values of the mass transfer rate coefficient.

The tracer plume center of mass moves at an average velocity which is independent of mass-transfer rate or migration distance, and can provide a useful metric for determining the number of pore volumes



required for tracer plume flushing. Average velocity can be calculated from Darcy flux provided the mobile and immobile porosity is known. Therefore, the average groundwater velocities are best to estimate pore volumes required for flushing. Calculations of pore volumes required for tracer flushing based solely on mobile pore-water velocity, apparent velocity for breakthrough of $C/C_0=0.5$ or other tracer velocities are scale and mass-transfer dependent, and may be less meaningful for describing flushing at the site scale.

Application of a dual-domain conceptual model to the ISPT is done within the context of a onedimensional flow field using the average velocity as a fitting parameter. At the ISPT, Well cluster PT-2 is located along a flow line hydraulically downgradient of the injection ROI. Velocity actually increases with distance toward the extraction wells. However, at the scale of flow between the injection well and PT-2, the variation in velocity is sufficiently small to be treated as a single uniform value. This assumption is suitable given the intended use of the results.

Application of CXTFIT to Tracer Data

The analysis was completed using the 1-D analytical model CXTFIT 2.1 which is an update and extension of the CXTFIT code of Parker and van Genuchten (1984) for estimating solute transport parameters using a nonlinear least-squares parameter optimization method. The program may be used to solve the inverse problem by fitting mathematical solutions of theoretical transport models to experimental results. This approach allows parameters in the transport models to be quantified. The program may also be used to solve the direct or forward problem to determine the concentration as a function of time and /or position. In this analysis, the direct approach is used.

The CXTFIT analytical model was used to simulate one-dimensional solute transport in a dual-domain system. The CXTFIT was applied to the ISPT tracer breakthrough data in order to provide a quantitative description of tracer flushing that has a strong basis in physical processes and to provide a more complete analysis of tracer data. Resulting simulations of each tracer test using similar values of the mass transfer rate coefficient provided an acceptable match to the movement of the center of tracer mass, and overall plume geometry observed for each injection. The dual-porosity model embodied in CXTFIT simulates tracer migration by advection and mass transfer between mobile and immobile pore spaces. A small realistic amount of hydrodynamic dispersion is considered in the analysis primarily to assure numerical stability of the solutions.

In the CXTFIT modeling exercise, the principle parameters used in calibrating CXTFIT were average tracer velocity, mobile and immobile porosity, and the mass transfer rate coefficient. To assure that values of average tracer velocity were consistent with site conditions, velocity was calculated from hydrogeologic (hydraulic conductivity, hydraulic gradient) and transport (mobile and immobile pore water velocity) parameters. Simulated results are compared with the observed breakthrough data by visual curve matching.

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The model boundaries and initial conditions are defined as shown in Figure A2. Previous hydrogeologic analysis of data from the dosing well clusters (PT-1 and PT-3) in the floodplain site provides a description of ROIs for various injections (Table A1). Previous hydrologic analysis also provides estimates of the appropriate mobile porosity value and reasonable values of velocity to use as initial estimates for calibration (ARCADIS 2008).

For defining the spatial model domain, it has been assumed that the location of the injection well is in the upgradient direction as defined in Figure A2. Therefore, the distance of PT-2D from the upgradient side of the injection ROI is its distance from PTI-1 plus the ROI. For the boundary condition time t=0 is the time when injection stops (start time for tracer drift) and at x=0, C=0 for all times. The dimensions of the area with initial $C = C_{injection}$ change for each tracer test because the ROI changes with each test. The area with initial $C = C_{injection}$ is centered on the injection well. These initial and boundary conditions used in this analysis represent an appropriate representation of actual conditions.

Once the initial and boundary values were defined, CXTFIT was run for individual injections. To proceed with curve matching, the mass transfer rate coefficient was set to a low value so dual-domain effects are minimal. Similarly the dispersivity was set to a minimal value. Initially, the front part of the breakthrough curve was matched based solely on advection by varying the velocity. Once this was completed, both velocity and the rate coefficient were varied to match the entire breakthrough curve based on advection-dispersion. The other hydrogeological parameters like porosity, hydraulic gradient and permeability's were also varied in successive simulations within the possible ranges for maximum curve matching.

During calibration, the concentration on the day of injection at PTI-1D was used to specify the initial concentration. However, the resulting simulated peak at PT-2D was overestimated by 20 to 30 percent. Actual concentration within the injection ROI was generally less than the injection concentration due to effects of diffusion into immobile pore space within the ROI. The difference between injection concentration within the ROI would depend on the concentration retained in the immobile pore space during previous injections. The first time a tracer was used at the site, the decrease in ROI concentration would be greater than during subsequent injections with the same tracer. Observed tracer data at the dosing wells provided confirmation of this hypothesis. Therefore, for subsequent calibration efforts, the initial concentration specified within the ROI was decreased from the injection concentration was decreased by 25 percent for all injections. However, for injection #1 and 4 the observed data shows a decrease of 70 to 80 percent of the initial concentration.

In addition to the curve matching exercise, for each breakthrough curve, the center of mass was calculated from the observed tracer concentration data in order to provide a measure of the observed average tracer velocity. This provided an additional constraint on the values of average tracer velocity used in the CXTFIT analysis.



Empirical Model of Tracer Flushing

For this analysis, only the trailing or elution portions of both simulated and observed curves were used. The time axis was transformed to a dimensionless pore volume number to assess the time required for flushing. The equation for the number of pore volumes (PV) that pass through a control volume during a certain time t is $PV=v_xt/L$, where, v is groundwater velocity and L is distance from PT-2D to the upgradient side of the ROI. The concentration axis is transformed to C/C_{max} . Pore-volume transformations were calculated separately both for mobile pore water velocity and average tracer velocity.

To fit the decay coefficient of the tracer, the recession curve after the inflection point was fitted to an exponential equation. Both the observed and simulated data are shown in Figure A4. The resulting decay coefficients for each simulated and observed injection are presented in Table A3.

Results and Interpretation

Physically-Based Model

The observed and corresponding simulated plots for the different injections are shown in Figure A3; the results confirm the validity of the dual domain conceptualization for solute transport. Estimated values of various parameters from CXTFIT analysis for different injections are presented in Table A2. The average value of estimated mass transfer rate coefficient is 0.02 per day and average pore water velocity is 3.7 feet/day. From the center of mass calculations, the average groundwater velocity is 0.9 feet/day.

The number of pore volume flushes necessary to achieve 95% reductions in contaminant concentration was then calculated using the dual domain model and the average parameter values determined from the tracer analysis. The initial normalized concentration within the model domain was assumed to be 100% and uniformly distributed, and concentration changes were simulated downgradient of a treatment zone. Complete treatment within the treatment zone and negligible contaminant sorption was assumed. The simulation results (Figure A5) indicate that 95% reduction in concentration is attained within approximately 2.0 pore volume flushes.

Empirical Model

The maximum, average values of all exponential decay coefficients (λ_e) derived from the empirical fitting analysis were 2.0 and 0.67 (as calculated from mobile pore volume expression). The number of pore volume flushes necessary to achieve 95% reduction in contaminant concentration (PV_{95%}) was calculated using the following empirical exponential decay model:

 $PV_{95\%} = -In(5\%)/\lambda_e$

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Based on the values indicated above, 95% reduction in concentration is attained after approximately 1.5 to 4.5 pore volume flushes. These values are consistent with the results obtained from the analysis using the physically-based model (two pore volume flushes). Because the tracer data confirm the dual domain conceptualization and constrain parameter values, the pore volume flushing value estimated by the physically-based modeling analysis is considered more reliable.

Conclusions

A technical basis for the number of pore volumes needed to attain cleanup goals by interpretation of tracer breakthrough data from the floodplain pilot tests was developed using tracer breakthrough data obtained during the Floodplain ISPTs. Both a physically-based dual-domain analytical model and an empirical model were used to analyze the tracer data.

The dual-domain model CXTFIT was used to interpret the tracer breakthrough data and estimate solute transport parameters values. Physically-based results of modeling the tracer migration and tailing support the conceptualization of solute transport as a dual-domain process. Using average parameter values derived from the interpretation of the tracer data, hypothetical chromium flushing downgradient of a treatment zone was then simulated. The results indicate that on average, clean water is achieved after 2.0 pore volume flushes, where clean water is defined as 95 percent reduction in concentration.

For the empirical analysis, an exponential model was fit to the trailing or elution portions of both the observed and CXTFIT-simulated curves. The fitted empirical decay coefficients were then used to calculate the number of pore volume needed to achieve 95% reduction in concentration. The empirical analysis resulted in range (1.5 to 4.5 pore volume flushes) that was consistent with the value derived from the physically-based model (2.0 pore volume flushes).

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Tables

- A1 Summary of Injection Tests
- A2 Summary of Aquifer Properties Estimated from 1-D Analytical Modeling

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A3 Summary of Half Life Analysis from Empirical Fitting

Figures

- A1 Site Map
- A2 Model Domain
- A3 Breakthrough Data and 1-D Modeling Fit Plots
- A4 Empirical Fit Between Observed and Simulated Data
- A5 Simulated Chromium Flushing Efficiency with Dual Domain Model

Table A1Summary of Injection TestsTopock Compressor StationTopock, California

Date	Solution (gal)	Tracer Type	Tracer Amount (Ibs)	Approximate Tracer Concentration (mg/L)	ROI from Hydrogeologic Analysis (ft)
5-May-06	6,000	Potassium Iodide	131	2,000	14.5
11-Aug-06	6,000	Fluorescein	0.33	5	14.5
7-Sep-06	6,000	Potassium Iodide	100	1,900	14.5
1-Nov-06	6,000	Fluorescein	0.33	5	14.5
7-May-07	19.000	Dotoccium Iodido	0.22	1.6	25.2
8-May-07	18,000	Polassium louide	0.55	1.0	20.0
17-Jul-07	18,000	Eluoroscoin	100	633	25.3
18-Jul-07	10,000	i iudiescelli	100	033	20.0

Notes:

gal = gallons lbs = pounds mg/L = milligrams per liter ROI = Radius of Injection ft = feet

Table A2 Aquifer Property Estimates for Topock Floodplain from 1-D Analytical Modeling Topock Compressor Station Topock, California

Paramotors	Injection #1		Injection #2		Injection #3		Injection #4		Injection #5		Injection #6		Average
F al allielei S	Input	Calculated	Values										
Mobile Porosity	0.07		0.08		0.12		0.12		0.07		0.07		0.09
Immobile Porosity	0.22		0.22		0.28		0.28		0.22		0.22		0.24
Total Porosity		0.29		0.3		0.4		0.4		0.29		0.29	0.33
Dimensionless Beta													
(ratio of mobile to		0.24		0.27		0.3		0.3		0.24		0.24	0.27
total porosity)													
Mass Transfer Rate	0.01		0.01		0.03		0.03		0.01		0.01		0.02
Coefficient (1/day)	0.01		0.01		0.00		0.00		0.01		0.01		0.02
Dimensionless													
Omega		0.04		0.04		0.09		0.09		0.04		0.04	0.06
(Sherwood/Peclet)													
Darcey Velocity		0.31		0.27		0.34		0.31		0.31		0.31	0.31
(ft/day)		0.01		0.2.		0.01		0.0.		0.01		0.01	
Groundwater													
Velocity, mobile		4.37		3.4		2.84		2.6		4.37		4.37	3.66
domain (ft/day)													
Average													
Groundwater	4.05				0.00		0.07		0.70		0.70		0.04
Velocity Calculated	1.05		1.44		0.88		0.67		0.72		0.72		0.91
from Center of Mass													
(ft/day)													
Average Fitted													
velocity		1.06		0.91		0.85		0.78		1.06		1.06	0.95
usea in CATFIT													
(ft/day)													

Notes:

ft/day = feet per day

Table A3 Half-Life Estimation of Concentration Decline Topock Compressor Station Topock, California

	Injection #1		Injection #2		Injection #3		Injection #4		Injection #5		Injection #6	
	Observed	1-D Analytical Solution										
Distance from upstream side of injection cylinder	59.30	59.30	59.30	59.30	59.30	59.30	59.30	59.30	70.00	70.00	70.00	70.00
Mobile pore-water porosity from 1-D analytical solution		0.07		0.08		0.12		0.12		0.07		0.07
Immobile pore- water porosity from 1-D analytical solution		0.22		0.22		0.28		0.28		0.30		0.22
Mass transfer rate (1/day)		0.01		0.01		0.03		0.03		0.01		0.01
Mobile pore velocity from 1-D analytical solution		4.37		3.40		2.84		2.60		4.37		4.37
Average tracer velocity from 1-D analytical solution (ft/day)		0.94		1.41		0.76		0.70		0.80		1.20
Maximum observed concentration	390,000	299,610	1,059	1,154	394,000	389,874	260	346	176,000	179,674	737	682
Time after injection to Cmax (days)	33	12	40	41	40	41	47	45	23	25	22	26
Time after injection to Cmax (mobile pore volumes)	1.56	0.02	1.35	1.40	1.35	1.40	1.54	1.45	0.08	0.23	0.02	0.29
Exponential decay coefficient for mobile pore volume expression (unitless)	-0.56	-0.33	-2.00	-0.62	-0.88	-1.01	-0.61	-0.97	-0.32	-0.41	-0.01	-0.41
Apparent half-life (mobile pore volumes)	1.24	2.08	0.35	1.12	0.79	0.69	1.15	0.71	2.15	1.70	61.3	1.70
Exponential decay coefficient for transformed time expression (1/days)	-0.04	-0.02	-0.11	-0.04	-0.04	-0.05	-0.03	-0.04	-0.02	-0.03	0.00	-0.03
Apparent half-life (davs)	17	28	6	20	16	14	26	16	34	27	990	27

Notes:

ft/day = feet per day

µg/L = micrograms per liter

Cmax = maximum concentration



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CONCENTRATIONS vs TIME PLOTS FOR DIFFERENT INJECTIONS PG&E TOPOCK FACILITY NEEDLES, CALIFORNIA

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Pore Volume

RECESSION CURVE AT PT-2D BASED ON MOBILE PORE-WATER VELOCITY PG&E TOPOCK FACILITY NEEDLES, CALIFORNIA

Pore Volume







Attachment B Analysis with Uplands In-situ Pilot Test Numerical Flow and Transport Model



TECHNICAL MEMORANDUM

Date: January 22, 2010 ARCADIS Project No.: RC000689.0001

Subject:

Technical Basis for Pore Volume Flushes for CMS Alternatives Modeling, Pacific Gas and Electric (PG&E) Compressor Station, Topock, California.

ATTACHMENT B - Analysis With Uplands In Situ Pilot Test Numerical Flow and Transport Model

Introduction

The purpose of this technical memorandum is to provide further technical support for the anticipated number of pore volumes needed to attain cleanup goals detailed in the Corrective Measures Study/Feasibility Study (CMS/FS). For this analysis, synthetic flushing curves were generated at fully screened target wells using the uplands pilot numerical flow and transport model (ARCADIS 2009). This model represents the area in the immediate vicinity of the Uplands In Situ Pilot Test area and was intended to support pilot test design and interpretation. As presented in detail in the Upland Reductive Zone In-Situ Pilot Test Final Completion Report (ARCADIS 2009), the model was previously calibrated to hydraulic and tracer data and included a detailed accounting of local geologic heterogeneity. These flushing curves were used to evaluate the anticipated relationship between clean water flushing and chromium concentration reduction following treatment.

Approach

As discussed in ARCADIS (2009) the hydraulic conductivity distribution and resulting advective flowfield dominated tracer and solute transport in the uplands pilot test. To adequately represent this behavior, the numerical model was discretized into 14 layers to explicitly capture heterogeneity, and tracer transport was successfully simulated with the advection-dispersion equation using a high porosity (i.e., equivalent to a dual-domain system with very high mass transfer) and minimal applied dispersivity.

This highly calibrated model was then used to simulate flushing behavior at synthetic fully screened target wells. For these simulations, a starting concentration of 100 percent was applied throughout the entire domain, and clean water (representing upgradient chromium treatment) was allowed to migrate from the upgradient boundary through the domain area (in these simulations, the pilot test wells were not operating). Two sets of synthetic flushing data were generated: one set for targets located in the middle of the model domain (designated as x = 1500 ft) and the second set for targets (designated as x = 3000 ft)

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located at the downgradient edge of the model. These curves represent the flushing efficiency associated with upgradient chromium treatment.

Results and Conclusions

The results are shown in Figure 1 below, where the predicted concentrations at the two target locations are plotted against the number of mobile pore volume flushes (Mobile PV). These results indicate that chromium concentrations will be reduced by 95 percent after approximately three pore volume flushes of clean water.



Figure B1. Model-generated chromium flushing curves.

References

ARCADIS. 2009. Upland Reductive Zone In-Situ Pilot Test Final Completion Report, Waste Discharge Requirements Order No. R7-2007-0015, PG&E Topock Compressor Station San Bernardino County, California. March 3, 2009