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Investigation of a Sustainable Approach to In-situ Remediation of Arsenic Impacted Groundwater





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CONTENTS

Executive Summary	v
1.0 Introduction	1-1
2.0 Site Characterization	2-1
2.1 Background	2-1
2.2 Soil Sampling	2-3
2.2.1 Soil Characterization – USACE, ERDC-EL	2-5
2.2.2 Soil Characterization – EPA/ORD	2-6
2.3 Groundwater Characterization	2-13
2.4 Biotic Oxidation of As(III)	2-15
2.5 Summary of Key Findings and Geochemical Modeling Approach	2-15
2.6 Quality Control/Quality Assurance	2-17
3.0 Bench Scale Tests	3-1
3.1 Background	3-1
3.2 Laboratory Tests and Results	3-3
3.2.1 Time to Equilibrium Tests	3-3
3.2.2 Sorption/Reaction Tests	3-7
3.2.3 Column Test	3-14
3.3 Model Simulations	3-21
3.3.1 Model Calibration to Batch and Column Test Data	3-21
3.3.2 Model Simulations of Field Conditions	3-26
3.4 Sources of Uncertainty	3-28
4.0 Summary and Conclusion	4-1
5.0 References	5-1



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FIGURES

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Figure 1.1	Geochemical zones and dissolved arsenic concentrations	1-3
Figure 2.1	Conceptual site model	2-2
Figure 2.2	Soil sampling locations ASB-1 and ASB-2	2-3
Figure 2.3	Percentage of sample mass recovered in the <425-micron size fraction	2-6
Figure 2.4	X-ray diffraction scans for samples from the ASB-1 and ASB-2 cores	2-8
Figure 2.5	FTIR spectra of samples ASB-1 27-28', ASB-1 28-29', ASB-2 26-27', and ASB-2 30-31'	2-9
Figure 2.6	Concentrations of total As (AsT) and As extracted with 0.1 M HCl and concentrations of extracted As present as As(III) and As(V)	2-10
Figure 2.7	SEM images and EDX maps of particles in samples ASB-1 27-28 and ASB-2 31-32	2-12
Figure 2.8	Pre and post air sparging dissolved iron and arsenic concentrations	2-14
Figure 3.1	Soil and groundwater collection locations	3-2
Figure 3.2	Time to equilibrium batch test results: Dissolved arsenic vs. time	3-5
Figure 3.3	Time to equilibrium batch test results: Dissolved iron vs. time	3-6
Figure 3.4	Sorption/reaction batch test results: Sand mixed with groundwater without pH adjustment	8-10
Figure 3.5	Sorption/reaction batch test results: Red/orange sand mixed with groundwater without pH adjustment	r 8-11
Figure 3.6	Sorption/reaction batch test results: Sand mixed with groundwater with pH adjustment	8-12
Figure 3.7	Sorption/reaction batch test results: Red/orange sand mixed with groundwater with pH adjustment	r 3-13
Figure 3.8	Column tests	8-15
Figure 3.9	Column tests results: Influent and effluent arsenic and iron concentrations 3	8-17
Figure 3.10	Column tests results: Influent and effluent arsenic speciation	8-18
Figure 3.11	Column tests results: Parameters measured in the laboratory	8-20
Figure 3.12	Sorption/reaction batch tests results: Comparison of modeled to measured iron and arsenic concentrations	8-23
Figure 3.13	Column tests: Comparison of modeled and measured results	8-25
Figure 3.14	Simulated iron concentration: Pre-air sparge conditions	8-27

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TABLES

Table 2.1	XRF soil analysis 2	-4
Table 2.2	EPA 6000/7000 series soil analysis 2	-5
Table 2.3	Sequential extraction results	-5
Table 2.4	Metals concentrations (mg/kg) in samples from locations ASB-1 and ASB-2 2	-7
Table 2.5	Concentrations of As and Fe (mg/kg), solid-phase As speciation (mg/kg), and recovery (%) in selected chemical extracts	10
Table 3.1	Soils used in batch and column tests	-1
Table 3.2	Time to equilibrium test results	-4
Table 3.3	Sorption/reaction batch test results using sand with a low iron content 3	-8
Table 3.4	Sorption/reaction batch test results using sand with a high iron content	-9
Table 3.5	Sorption/reaction batch test results using sand with a low iron content and pH adjustment	-9
Table 3.6	Sorption/reaction batch test results using sand with a high iron content and pH adjustment	-9
Table 3.7	Column test analytical results 3-1	16
Table 3.8	Column test laboratory measured parameters	19

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EXECUTIVE SUMMARY

The Vineland Chemical Company operated from 1949 to 1994 producing arsenical herbicides and fungicides. A Record of Decision (ROD) signed in 1989 addressed remedial actions at the site which included a pump and treat (P&T) system to remediate arsenic in groundwater. A Remediation System Evaluation (RSE) optimization study conducted in 2010, ten years after the onset of the P&T system, found that the current P&T system was unlikely to restore the aquifer within a reasonable time period as specified by the ROD. Because the annual cost for the P&T system is very high, the study listed several recommendations designed to optimize or replace the P&T system, including in-situ remediation for arsenic immobilization. The challenges of operating the P&T system at the Vineland Chemical Company site created an opportunity to find a sustainable in-situ approach to remediate arsenic and identify the key processes involved.

A large-scale pilot air sparge system was developed in response and began operation in 2015. After several years of operating the pilot system, results showed that arsenic in iron-rich groundwater was immobilized successfully. Key processes and parameters controlling arsenic immobilization were determined through a novel approach that combined bench-scale tests, geochemical modeling, and groundwater and soil characterization. Results from these tests can be used to optimize the design and operation of the fullscale system and provide guidance for the design of air sparge systems at other sites with arsenic-impacted iron-rich groundwater at variable redox conditions.

Field data from the large-scale air sparge system show that arsenic and iron were reduced from levels around 1,000 and 15,000 μ g/L to levels as low as 10 and 1,000 μ g/L, respectively, in specific areas. Key processes that account for arsenic immobilization in groundwater include:

- Oxidation and precipitation of iron to amorphous hydrous ferric oxide (HFO) This process was modeled as a function of dissolved oxygen (DO) and pH using a non-equilibrium kinetic rate equation. Iron precipitation does not occur instantaneously at the pH range of 5.5 to 6.5 encountered at this site. Precipitation of HFO occurred downgradient of the air sparge wells prior to reaching compliance points, reducing the need for well maintenance due to clogging.
- Sorption of arsenic to amorphous HFO and iron in soil This process was modeled using the surface complexation model available in PHREEQC. The majority of arsenic was immobilized by the freshly oxidized iron with a small fraction of arsenic immobilized by iron in soil. Soil and groundwater characterization demonstrated that oxidation of arsenic was not required for arsenic immobilization because the reduced form of arsenic was found to be the dominant species in both the aqueous and solid (immobilized) phases in the area of the pilot study.
- **Degassing of CO**₂ The pH of groundwater is controlled by opposing processes: oxidation of iron and degassing of CO₂. Iron oxidation decreases pH and air sparging reduces CO₂ concentrations which lowers the concentration of carbonic acid and results in a pH increase.

Identifying the processes responsible for arsenic immobilization was an important factor in the sustainable operation of the air sparge system. Air sparging for arsenic immobilization can be applied to other sites where iron is present in groundwater in sufficient quantities, and a similar procedure of groundwater and soil characterization combined with bench-scale testing and modeling can be applied to identify the parameters most influential on pH and iron oxidation rate.



The presence of arsenic in water and soil is a global concern since it is identified as a carcinogen and presents a serious threat to human health. Despite the rise in scientific research in this area, remediation of arsenic contamination in groundwater is mostly done by ex-situ methods, whereas more sustainable in-situ methods often do not receive consideration.

The ongoing remedial activities at the Vineland Chemical Company Superfund Site in New Jersey provided a unique opportunity to address arsenic contamination in groundwater using an in-situ approach. The Vineland Chemical Company operated from 1949 to 1994 producing arsenical herbicides and fungicides, resulting in the contamination of soil and groundwater. A ROD signed in 1989 addressed remedial actions at the site, which included a pump and treat (P&T) system to remediate arsenic in groundwater. An RSE optimization study conducted in 2010, ten years after the onset of the P&T system, found that the current P&T system was unlikely to restore the aquifer within a reasonable time period as specified by the ROD. Because the annual cost for the P&T system, including in-situ remediation for arsenic immobilization. Air sparging was ultimately selected to immobilize arsenic in-situ after a series of bench scale treatability studies were conducted (Sehayek et al., 2014b).

Successful in-situ remediation of arsenic contaminated sites requires a thorough understanding of the factors influencing arsenic transport as well as the ability to predict the behavior of arsenic in soils and aquifer systems under future conditions (Bundschuh and Bhattacharya, 2014). The overall goal of this study is to understand and, when possible, quantify the processes controlling the fate and transport of arsenic under ambient, as well as, under redox conditions created downgradient of an air sparge system. Previous testing has shown that the ambient geochemical composition of groundwater along the arsenic plume can be divided into three general categories (Sehayek et al., 2014a).

- Anoxic (with DO < 1 mg/L), arsenic-impacted and iron-rich groundwater located along the leading edge of the arsenic plume that discharges to ponds and a stream (the Blackwater Branch),
- 2. A mixture of oxic groundwater and the anoxic arsenic-impacted iron-rich groundwater located in the middle of the arsenic plume along the segment where it partially discharges to a surface water body, and
- 3. Arsenic impacted iron deficient oxic/anoxic groundwater located near the source.

The areas of the site where these three geochemical zones exist are shown on Figure 1.1 along with the arsenic plume in (a) the lower portion of the surficial aquifer (well depths ranging between 25 and 75 ft below ground surface) and (b) the upper portion of the surficial aquifer (well depths ranging between 13 and 35 ft below ground surface). The mechanisms controlling the fate and transport of arsenic could be different within each of these zones, but changes in the project limited the study area to the leading edge of the arsenic plume where conditions prior to air sparging were anoxic and iron-rich (category 1 above). Because the air sparge pilot was located along the leading edge of the arsenic plume, this study addressed the overall objective of qualifying and quantifying processes taking place under ambient conditions and under air sparge conditions.

The following tasks were performed to accomplish the goals of the study:

Task 1 – Quantification of Abiotic Processes – This task included characterization of groundwater and soil, batch bench-scale tests, and development of a quantitative tool that accounts for arsenic partitioning to the solid phase using the geochemical model PHREEQC. Soil and groundwater for characterization and bench-scale testing were collected from locations on the site that reflected the geochemical conditions of interest along the leading edge of the arsenic plume.

Task 2 – Determine whether biotic oxidation of arsenite (As(III)) is taking place – This task included determining whether the genes *aioA (aerobic arsenite oxidation)* and/or *arxA (anaerobic arsenite oxidation)* involved in As(III) oxidation can be detected in groundwater or soil samples obtained from the Vineland Chemical Company Superfund site. Task 2 was implemented using soil and groundwater samples from the leading edge of the arsenic plume.

Task 3 – Fate and transport of arsenic – This task included performing column tests to determine whether the quantitative tool developed in Task 1 can be used to conservatively predict the fate and transport of arsenic in the columns and subsequently applied to predict the fate and transport of arsenic in the field.

These tasks were accomplished as part of ongoing remedial actions and supported by EPA/ORD funding through the Superfund Technology Liaison (STL) Extramural funding program. This report summarizes the work performed by the U.S. Army Corps of Engineers (USACE), the Environmental Protection Agency (EPA) Office of Research and Development (ORD), and EPA Region 2.



Figure 1.1 Geochemical zones and dissolved arsenic concentrations: (a) lower portion of surficial aquifer; (b) upper portion of surficial aquifer.



2.1 Background

The geology at the Vineland Chemical Company Site consists of an upper sand unit that has been conceptually divided into an upper zone and lower zone known at the site as the shallow aquifer and mid-depth aquifer. In many locations, iron staining and iron-cemented sands were noted at the base of the mid-depth aquifer. A banded zone consisting of interbedded clays and silts lies underneath the mid-depth aquifer. Below the banded zone is an oxic zone known as the middle sand unit. A schematic of the conceptual site model is shown in Figure 2.1.

Oxic water from the middle sand unit upwells to the mid-depth aquifer in a portion of the site where the silts and clays of the banded zone are discontinuous or missing. The oxic water dissolves pyrite minerals that are found at the bottom of the mid-depth aquifer and in the banded zone, where present, resulting in groundwater that has a high dissolved iron concentration and a low pH. At times, the hydraulic conditions at the site result in oxic conditions after water from the middle sand unit has mixed with water from the upper sand unit. These oxic conditions cause iron to precipitate out of solution, forming iron minerals that have been detected during previous field investigations (Sehayek et al., 2014a).



Historical investigations conducted at the site included soil sampling in the upper sand and banded zone. Iron minerals detected in the iron-stained soil of the mid-depth aquifer using X-ray diffraction (XRD) included goethite, hematite, magnetite, and/or maghemite. The iron-bearing mineral most frequently encountered was goethite. Goethite was also reported to be present at highest percent weight compared to other iron minerals. Historical investigations included sampling and analysis for iron in soil as 'amorphous oxides' using either citrate-bi-carbonate dithionite or oxalate extractions. Results of these investigations show that the percent of iron as 'amorphous oxides' in the soil was negligible (<0.2 wt%). These historical investigations also detected pyrite in the clay layer located at the base of the mid-depth aquifer.

Previous investigations also included analysis for arsenic metals and minerals. Results of these investigations indicated that the highest arsenic concentrations were encountered in the saturated zone of the mid-depth aquifer within the iron-stained or cemented soil, suggesting that arsenic removal often coincides with iron oxidation and precipitation. Arsenic was not encountered in the intervals containing pyrite.

The DO that is naturally available in the groundwater at the Vineland Chemical Company site is often not sufficient to precipitate all of the dissolved iron from solution, resulting in high-iron, low-oxygen, and high-arsenic conditions along the downgradient edge of the arsenic plume. Soil and groundwater characterization along the leading edge of the arsenic plume was implemented as part of Task 1.

2.2 Soil Sampling

A soil sampling program was implemented in an attempt to gain direct evidence of the minerals that are formed under in-situ air sparge conditions. Soil samples were collected from two different locations along the downgradient edge of the groundwater plume; one location was hydraulically upgradient of the air sparge area (ASB-1 shown on Figure 2.2) and one location was impacted by air sparging (ASB-2 shown on Figure 2.2). Soil boring ASB-1 was completed next to piezometer PZ-9 where the arsenic concentration in groundwater is approximately 1,000 μ g/L. Soil boring ASB-2 was completed next to piezometer PZ-10 where air sparging has decreased the arsenic concentration in the groundwater from approximately 1,000 μ g/L to 10 μ g/L. In addition to the decrease in groundwater arsenic concentration, the impact of the air sparging was demonstrated by changes in iron minerology.



Figure 2.2 Soil sample locations ASB-1 and ASB-2.

Beginning at a depth of approximately 25 ft below land surface, XRF was used to approximate the arsenic and iron concentrations of the soil collected from each boring at one-foot intervals. XRF results for arsenic and iron concentrations in soil for ABS-1 and ABS-2 are summarized in Table 2.1. Soil sample intervals with the highest arsenic concentrations in each boring (four from ASB-1 and three from ASB-2, as indicated on Table 2.1) were selected for additional characterization. Each of the seven one-foot sample intervals selected for additional characterization was split in half. One half was shipped to the USACE Engineer Research and Development Center Environmental Laboratory (ERDC-EL), and the other half was shipped to the Environmental Protection Agency Office of Research and Development (EPA/ ORD). Soil tests performed by ERDC-EL and EPA/ORD and the results are summarized in Sections 2.2.1 and 2.2.2, respectively.

Table 2.1 X	Table 2.1 XRF soil analysis																		
Location	Soil Description	Date	Depth Interval	San Ty Colle	nple pe ected		XRF Result (Arsenic, ppm) ²						XRF Result (Iron, %)						
Identification	Son Description	Collected	(ft bgs)	XRF only	XRF and LAB ¹	Result RUN 1	+/-	Result RUN 2	+/-	Result RUN 3	+/-	AVERAGE	Result RUN 1	+/-	Result RUN 2	+/-	Result RUN 3	+/-	AVERAGE
ASB-1	sand with gravel	4/6/2016	25.0-26.0	х		15	2	12	2	10	2	12	0.19	0.03	0.16	0.03	0.16	0.03	0.17
ASB-1	sand with clay	4/6/2016	26.0-27.0		х	193	5	230	5	142	4	188	4.10	0.10	4.70	0.10	2.80	0.10	3.87
ASB-1	iron-stained sand (between clay layers)	4/6/2016	27.0-28.0		х	321	6	364	7	443	8	376	4.91	0.10	6.39	0.06	8.36	0.08	6.55
ASB-1	iron-stained sand with clay	4/6/2016	28.0-29.0		х	348	7	408	7	297	6	351	4.53	0.10	6.03	0.06	3.46	0.10	4.67
ASB-1	iron-stained sand	4/6/2016	29.0-30.0		х	186	4	186	4	172	4	181	1.93	0.10	1.85	0.10	1.68	0.10	1.82
ASB-1	iron-stained silty/wet sand	4/6/2016	30.0-31.0	х		126	4	108	3	105	3	113	1.55	0.10	1.27	0.10	1.15	0.10	1.32
ASB-1	iron-stained sand	4/6/2016	31.0-32.0	х		52	3	41	3	46	3	46	1.01	0.10	0.87	0.10	1.05	0.10	0.98
ASB-1	clay	4/6/2016	32.0-33.0	х		37	3	32	3	49	3	39	2.22	0.10	2.52	0.10	2.42	0.10	2.39
ASB-1	slightly stained sand with clay	4/6/2016	33.0-34.0	х		< 6.0	-	< 6.0	-	< 6.0	-	< 6.0	1.84	0.10	1.00	0.10	0.72	0.08	1.18
ASB-1	slightly stained sand	4/6/2016	34.0-35.0	х		7	2	< 6.0	-	< 6.0	-	< 4	0.76	0.08	0.60	0.07	0.43	0.06	0.60
ASB-1	slightly stained sand	4/6/2016	35.0-36.0	х		< 6.0	-	< 5.4	-	< 5.6	-	< 5.7	0.38	0.20	0.48	0.06	0.29	0.04	0.38
ASB-1	slightly stained sand	4/6/2016	36.0-37.0	х		< 5.7	-	< 5.7	-	< 5.9	-	< 5.8	0.38	0.05	0.41	0.05	0.41	0.05	0.40
ASB-1	clay	4/6/2016	37.0-38.0	х		14	2	7	2	8	2	10	4.13	0.10	2.19	0.10	0.95	0.10	2.42
ASB-1	sand	4/6/2016	38.0-39.0	х		< 5.5	-	< 5.6	-	< 5.4	-	< 5.5	0.33	0.04	0.43	0.05	0.38	0.05	0.38
ASB-1	sand with clay	4/6/2016	39.0-40.0	х		< 6.0	-	6	2	< 6.0	-	< 4	1.42	0.10	1.42	0.10	0.8625	0.09	1.23
ASB-2	sand with gravel	4/5/2016	25.0-26.0	x		33	2	30	2	24	5	29	0.31	0.10	0.28	0.10	0.31	0.10	0.30
ASB-2	sand with gravel	4/5/2016	26.0-27.0		х	137	4	140	5	179	5	152	4.12	0.10	4.80	0.10	4.01	0.10	4.31
ASB-2	sand	4/5/2016	27.0-28.0	х		40	4	47	3	51	3	46	1.16	0.10	1.51	0.10	1.44	0.10	1.37
ASB-2	sand	4/5/2016	28.0-29.0	х		54	3	50	3	44	5	49	1.07	0.10	0.86	0.10	1.02	0.10	0.98
ASB-2	sand	4/5/2016	29.0-30.0	х		93	3	89	3	102	4	95	2.25	0.10	1.71	0.10	1.53	0.10	1.83
ASB-2	slightly stained sand	4/5/2016	30.0-31.0		х	118	4	179	4	73	3	123	2.21	0.10	2.91	0.10	1.47	0.10	2.20
ASB-2	iron-stained sand	4/5/2016	31.0-32.0		х	150	5	81	3	104	4	112	2.25	0.10	1.16	0.10	1.53	0.10	1.65
ASB-2	iron-stained sand	4/5/2016	32.0-32.5	x		87	3	76	3	101	3	88	1.19	0.10	1.08	0.10	1.58	0.10	1.28
ASB-2	silty sand	4/5/2016	32.5-33.0	х		27	3	25	3	27	2	26	1.03	0.10	1.01	0.10	1.02	0.10	1.02
ASB-2	sand	4/5/2016	33.0-34.0	х		10	2	12	2	8	2	10	0.48	0.06	0.71	0.08	0.65	0.07	0.62
ASB-2	sand	4/5/2016	34.0-35.0	х		< 7.0	-	< 5.8	-	< 7.0	-	< 6.6	0.94	0.10	0.94	0.10	1.45	0.10	1.11
ASB-2	wet sand	4/5/2016	35.0-36.0	х		< 5.4	-	< 5.6	-	< 5.5	-	< 5.5	0.51	0.06	0.58	0.06	0.62	0.07	0.57

¹Soil samples sent to the USACE's Engineering Research and Development Center (ERDC) laboratory in Vicksburg, Mississippi for analysis ²For instances where an interval had both detected and non-detect results between runs, half the detection limit was used for the average calculation

ft bgs = feet below ground surface; N/A = not applicable; ppm = parts per million; XRF = X-ray fluorescence

2.2.1 Soil Characterization – USACE, ERDC-EL

Soil characterization at USACE, ERDC-EL included metal analysis using EPA 6000/7000 series method, XRD, and sequential chemical extraction.

Arsenic and iron concentrations in soil determined by EPA 6000/7000 series method are provided in Appendix A and summarized in Table 2.2. The ranges in arsenic and iron concentrations of soil samples collected from ASB-1 were 170 to 567 mg/kg, and 21,600 to 50,200 mg/kg, respectively. The arsenic and iron contents at sample location ASB-2 were slightly lower, with arsenic concentrations ranging from 83.9 to 94.7 mg/kg and iron concentrations ranging from 10,100 to 22,000 mg/kg. The results from the laboratory analysis were within reasonable agreement to the concentrations determined in the field using XRF (see Table 2.1).

Table 2.2 El	Table 2.2 EPA 6000/7000 series soil analysis											
Location	Soil Description	Date Collected	Depth Interval	As	Fe							
Identification	Son Description	Dute concetted	(ft bgs)	(mg/kg)	(mg/kg)							
ASB-1	sand with clay	4/6/2016	26.0-27.0	170	22600							
ASB-1	iron-stained sand	4/6/2016	27.0-28.0	519	50200							
ASB-1	iron-stained sand with clay	4/6/2016	28.0-29.0	567	45300							
ASB-1	iron-stained sand	4/6/2016	29.0-30.0	229	21600							
ASB-2	sand with gravel	4/5/2016	26.0-27.0	94.7	22000							
ASB-2	slightly stained sand	4/5/2016	30.0-31.0	88.3	11800							
ASB-2	iron-stained sand	4/5/2016	31.0-32.0	83.9	10100							

As = Arsenic; Fe = Iron; ft bgs = feet below ground surface; mg/kg = milligram per kilogram

Sequential extraction was performed by USACE, ERDC-EL to determine the fraction of arsenic and iron in the soluble, exchangeable, carbonate, Fe-Mn oxides, organic matter and sulfide, and residual forms. Results from sequential extractions are provided in Appendix A and summarized in Table 2.3. The analyses showed that a negligible amount of arsenic was soluble, and the majority of the arsenic and iron were associated with the oxide and the stable residual components. Arsenic was not detected under the exchangeable and organic matter and sulfide extractions.

Table 2.3 Se	Table 2.3 Sequential extraction results											
Location	Depth Interval	Carbo	onate	Ox	ide	Resi	dual	Soluble				
Identification	(ft bgs)	As (mg/kg)	Fe (mg/kg)	As (mg/kg)	Fe (mg/kg)	As (mg/kg)	Fe (mg/kg)	As (mg/kg)	Fe (mg/kg)			
ASB-1	26.0-27.0	7.02	7.95	44.8	1150	33.4	4530	2.92	54.4			
ASB-1	27.0-28.0	19.4	20.9	104	923	62.9	6780	8.18	25.9			
ASB-1	28.0-29.0	24.3	10.8	92.9	1270	108	8750	10	5.58			
ASB-1	29.0-30.0	13.7	9.78	74.9	524	38.6	4400	5.31	24			
	20.0.27.0	0.005	10.0	C 42	017	10	4250	ND	24.6			
ASB-2	26.0-27.0	0.665	10.9	6.42	817	18	4250	ND	34.6			
ASB-2	30.0-31.0	0.636	7.46	6.15	412	14.9	2090	ND	35.9			
ASB-2	31.0-32.0	3.66	11.2	23.2	427	14.1	1850	1.4	78.8			

As = Arsenic; Fe = Iron; ND = Not detected; ft bgs = feet below ground surface; mg/kg = milligram per kilogram

XRD results are provided in Appendix B. Results indicate that the most frequently encountered form of iron mineral is goethite. The less stable form of iron mineral, ferrihydrite, also defined in some places as the dried form of amorphous ferric hydroxide (i.e. hydrous ferric oxides or HFO), was encountered only in one interval located in the air sparge area (specifically boring ASB-2 interval 26-27'). The limited detection of ferrihydrite in the current and historical field investigations and the high frequency and quantity, expressed by percent weight, of the more thermodynamically stable and more crystallized goethite suggests that iron oxidation results in the formation of amorphous ferric oxide which transforms over time to the more stable goethite or other iron minerals.

Hematite, was detected by USACE, ERDC- EL only in one soil sample. EPA/ORD detected hematite in all soil samples. The discrepancy between EPA/ORD and the USACE, ERDC-EL can be attributed to the faster scan speed used by USACE, ERDC-EL and the lower relative mass of hematite as compared to goethite.

2.2.2 Soil Characterization – EPA/ORD

Soil characterization at EPA/NRMRL/ GWERD included XRD; Fouriertransform infrared spectroscopy (FTIR); scanning electron microscopy (SEM); energy dispersive X-ray spectrometry (EDX); and metals analysis using microwave digestion, targeted chemical extractions, and arsenic speciation using liquid chromatography (LC) coupled on-line to ICP-mass spectrometry (LC-ICP-MS).

Samples from locations ASB-1 and ASB-2 were prepared in an anaerobic glovebox (Coy Inc.) with a maintained N₂ plus 5% H₂ atmosphere. Samples were allowed to dry for two weeks within the glovebox at ambient conditions aided by alumina desiccant plates. The dried samples were disaggregated using an agate mortar and pestle and sieved to recover aquifer particles in the <40 mesh size range (<425 micron). For each sample, mass recovery in the <40 mesh sieve is shown on Figure 2.3.



Figure 2.3 Percentage of sample mass recovered in the <425 micron size fraction.

Solid-phase concentrations of metals in the bulk and <40 mesh size fraction were determined using microwave-assisted digestion and inductively coupled plasma – optical emission spectrometry (ICP-OES) following EPA Method 200.7. A certified reference material from ERA (Golden, CO; cat. #540) was analyzed along with the sample batch and all QC performance acceptance limits were met, except for uranium and silver. For these elements, mass concentrations determined were low by up to 10% compared to the certified values. Solid-phase concentrations for selected elements are provided in Table 2.4. In all cases where an analyte was detected, concentrations were greater in the fine-grained fraction (<425 micron) compared to the bulk sample, which is expected. Across all of the samples, iron concentrations ranged from about 0.55 to 7.37 wt%; arsenic concentrations ranged from 53 to 465 mg/kg. Overall, these metals concentrations are in reasonable agreement with results of XRF and digestion analyses presented in Tables 2.1 and 2.2.

Table Conc	Concentrations in the bulk and fine (<40 mesh) fractions are designated as b and f, respectively													
				AS	B-1						AS	B-2		
	26-b	26-f	27-b	27-f	28-b	28-f	29-b	29-f	26-b	26-f	30-b	30-f	31-b	31-f
AI	2855	6725	2224	7600	4870	7417	1300	1386	324	6350	434	855	324	960
Са	12 J	25 J	9 J	30 J	18 J	27 J	5 J	6 J	46	79	<40 U	8 J	<40 U	8 J
Mg	62	117	21 J	58	126	154	12 J	14 J	57	84	<40 U	5 J	<40 U	8 J
Fe	24690	44890	27190	73660	26740	36970	13350	14310	19150	32460	5800	9350	5520	14390
Mn	<8 U	<8 U	4 J	20	<8 U	<8 U	<8 U	<8 U						
As	201	357	311	465	309	389	159	174	65	95	53	87	58	146
Pb	<8 U	11	<8 U	15	<8 U	11	<8 U	<8 U	<8 U	10	<8 U	<8 U	<8 U	<8 U
Cd	3 J	6	3 J	8	3 J	4	1 J	2 J	2 J	4	<4 U	1 J	<4 U	2 J
Ni	<4 U	1 J	<4 U	1 J	<4 U	2 J	<4 U	<4 U	<4 U	1 J				
v	7	13	6	13	18	22	6	6	31	47	2	4	2	5

Concentrations determined using microwave-assisted sample digestion and ICP-OES analysis following EPA Method 200.7.

Data qualifiers: J, analyte was detected above the method detection limit (MDL) but below the quantitation limit (QL). U, analyte was not detected.

XRD analyses were carried out using a Rigaku Miniflex II diffractometer with Mn-filtered FeKα radiation (λ = 0.1937 nm). Diffraction data were collected from 5° to 90° 20 with 0.01° 20 step increments at a scan rate of 6 s per step. NIST 640b standard reference material (silicon powder) was periodically scanned as a quality control check of d-spacing accuracy. Data collected from the XRD scans were imported into the Jade (Materials Data, Inc.) software package for analysis and matched to the Powder Diffraction File Data Base (PDF, International Centre for Diffraction Data). XRD scans for all core samples (<40 mesh size fraction) are shown on Figure 2.4. The dominant mineral components identified were quartz, kaolinite, goethite, and hematite. Similar results were obtained by USACE, although hematite was less frequently identified in the samples. This finding is attributed to the fact that EPA/ORD used the <40 mesh size fraction in their analysis and adopted a slower scan rate in the XRD analysis to improve sensitivity. Ferrihydrite (hydrous ferric oxide) was not detected in the XRD scans, but identification of this poorly crystalline material in the presence of other strongly diffracting sample components is notoriously difficult. A further attempt was made by ultra-sounding the <40 mesh size fraction in methanol and collecting the dispersed particulates in suspension. Again, quartz, kaolinite, goethite, and hematite were detected (results not shown), but kaolinite was more abundant and illite was identified in several samples (ASB-1 28-29; ASB-2 26-27; ASB-2 30-31).



cores (<40 mesh size fraction).

FTIR spectra were collected with a Bruker Vertex 70 spectrometer. Samples were prepared as pellets with KBr (weight ratio 195 mg KBr to 5 mg sample). Samples were scanned 32 times from wavenumber 400-4000 cm⁻¹. As a quality control check, calcium carbonate was scanned and results were compared with spectral data from Adler and Kerr (1962). FTIR spectra for selected samples are shown in Figure 2.5 and results are consistent with XRD analyses in showing the presence of kaolinite and goethite in the samples. Arsenic sorbed onto iron oxide surfaces typically shows an absorption band at about 1617 cm⁻¹ (Hsia et al., 1993). No absorption features could be attributed to arsenic in the measured spectra which indicates that the resolution of the method requires higher arsenic surface loadings.



Figure 2.5 FTIR spectra of samples ASB-1 27-28', ASB-1 28-29', ASB-2 26-27', and ASB-2 30-31'.

More sensitive chemical extraction tests were conducted under anaerobic conditions using deoxygenated water and 0.1 M HCl. Water extractions were expected to dissolve the most labile forms of arsenic in the samples and 0.1 M HCl was expected to extract poorly crystalline hydrous ferric oxides and associated arsenic (e.g., Kostka and Luther, 1994). Note that dilute HCl is not expected to dissolve goethite and/or hematite, but will dissolve hydrous ferric oxide. Solidphase concentrations of arsenic measured are shown on Figure 2.6 and Table 2.5. In core ASB-1, waterextractable arsenic ranged from 23 to 119 mg/kg, representing about 9 to 25% of the total arsenic; in core ASB-2, water-extractable arsenic ranged from 2 to 12 mg/kg, or about 2 to 10% of the total arsenic. Solid-phase arsenic concentrations determined using 0.1 M HCl ranged from 44 to 881 mg/kg, and, in most cases, the majority of the arsenic was recovered using 0.1 M HCl. This finding suggests that much of the solid-phase arsenic is associated with poorly crystalline iron-bearing materials.



Note: Most of the As was present as As(III). Concentrations of total Fe (FeT) and Fe extracted with 0.1 M HCl. Note dilute HCl is not expected to dissolve goethite and/or hematite but is expected to dissolve poorly crystalline hydrous ferric oxides.

Figure 2.6 Concentrations of total As (AsT) and As extracted with 0.1 M HCI and concentrations of extracted As present as As(III) and As(V).

selected ch	emical	extract	S							
Sample	As Total	As H₂O	As 0.1 M HCl	As Recovered	As As(III) As(III) As(V) Fe Fe vered H2O 0.1 M HCI 0.1 M HCI Total H2O + 0.1 M HCI Rd		Fe Recovery			
	mg/kg	mg/kg	mg/kg	%	mg/kg	mg/kg	mg/kg	wt%	wt%	%
ASB-1 26-27	357	34	276	87	58	224	20	4.49	0.29	6.4
ASB-1 27-28	465	119	881	215	120	663	54	7.37	0.71	9.6
ASB-1 28-29	389	38	317	91	61	227	30	3.70	0.30	8.1
ASB-1 29-30	174	23	97	69	25	88	10	1.43	0.06	4.2
					_					
ASB-2 26-27	95	1.5	44	48	1.2	7.9	22	3.25	0.19	5.8
ASB-2 30-31	87	9.1	52	70	5.0	28	4.8	0.94	0.07	7.4
ASB-2 31-32	182	12	62	41	7.6	46	7.3	1.84	0.09	4.9

Table 2.5 Concentrations of As and Fe (mg/kg), solid phase As speciation (mg/kg), and recovery (%) in selected chemical extracts

The sequential extraction testing performed by ERDC (Section 2.2.1) similarly found that a significant portion of the arsenic was associated with iron oxides, but those results also suggested that a notable fraction of the arsenic remained in the stable residual form. It is unknown if the discrepancy between the results proposed by EPA/ ORD and the results proposed by ERDC are a result of the extraction method, sample preparation/handling (e.g. use of bulk vs. <40 mesh size fraction), or mineralogical differences in the soil sub-samples sent to each lab. The differences in the fraction of arsenic found to be associated with the poorly crystalline iron-bearing minerals has implications for desorption of arsenic but should not impact the interpretation of arsenic sorption mechanisms.

The distribution of arsenate and arsenite species in the water and 0.1 M HCl extracts was determined using liquid chromatography (LC) coupled on-line to ICP-mass spectrometry (LC-ICP-MS; Thermo Electron Spectra HPLC) using collision cell technology to remove spectral interferences. Samples for arsenic speciation were filtered, acidified with HCl (pH<2; Optima, Fisher Scientific), and retained chilled in amber-plastic bottles. Chromatographic separation of arsenic species was accomplished using a PRP-X100 guard column (Hamilton), a PRP-X100 separator column (Hamilton), and by pumping an isocratic eluent [1.0 mL min⁻¹, 10 mM (NH₄)H₂PO₄/NH₄NO₃]. Eluent was directly aspirated into a Thermo Electron X series II ICP-MS and arsenic was detected by monitoring the m/z = 75 signal. In core ASB-1, most of the extracted arsenic (88-92%) was present as As(III). Similar results were obtained for samples from core ASB-2 [26-86% As as As(III); Table 2.5], although the fraction of As as As(V) increased at shallower depth intervals.

SEM-EDX results are shown in Fig. 2.7 for samples ASB-1 27-28 and ASB-2 31-32. In both samples, arsenic was found at low concentrations (<2 wt%) associated with iron-rich coatings on aquifer particles. These results show that at the micro-scale, arsenic is associated with iron and is found mainly associated with particle coatings.





Figure 2.7 SEM images and EDX maps of particles in samples ASB-1 27-28 and ASB-2 31-32.

2.3 Groundwater Characterization

Groundwater was sampled prior and during air sparging and analyzed for total and dissolved metals and for arsenic speciation. Significant observations from the groundwater sampling program that took place between the fall of 2015 and the spring of 2016 are described below.

- Prior to air sparging, the dissolved arsenic concentrations were approximately 1 mg/L adjacent to the air sparge wells. During air sparging, the most significant decrease in arsenic was observed approximately 15 ft downgradient of the air sparge line where dissolved arsenic dropped to 0.007 mg/L. Arsenic concentrations in a monitoring well located approximately 40 ft downgradient of the air sparge wells dropped to 0.234 mg/L, below the alternate concentration limit (ACL) of 0.350 mg/L stipulated in the 1989 ROD. The arsenic concentration in the well located about 100 feet downgradient dropped from 1 mg/L to 0.388 mg/L (slightly above the ACL).
- Prior to air sparging, dissolved iron concentrations ranged between about 15 to 20 mg/L. During air sparging, iron concentrations declined to a range of 0.3 to 3 mg/L downgradient of the air sparge line.
- Prior to air sparging, the groundwater was anoxic with DO concentrations less than 1 mg/L and the oxidation reduction potential (ORP) in the arsenic-impacted area ranged between approximately -50 and -125 mV. These DO and ORP values are indicative of iron-reducing conditions. During air sparging, the DO concentrations increased to between 2 and 11 mg/L and ORP increased to approximately 100 mV to 300 mV.
- Historical pH levels in the area adjacent to the air sparge wells ranged between about 4.5 and 6, with the majority of the readings between 4.5 and 5.5. In general, during air sparging, the pH slightly increased to values between 5.5 and 6. Oxidation and precipitation of iron is expected to result in decreasing pH; however, the pH during air sparging slightly increased. Previous investigations at the site and geochemical modeling indicate that groundwater at the site is supersaturated with carbon dioxide (CO₂). The air sparging resulted in a release of gases into surface water bodies at distances greater than 50 feet. This resulted in degassing of CO₂ and a consequent increase in pH. The source of CO₂ is believed to be biological activity in the clay layer at the base of the aquifer. This layer contains high total organic carbon (TOC) of about 100 mg/kg.
- The ORP of anoxic groundwater is often controlled by the iron chemistry. The pH and ORP measured in four existing piezometers were plotted on an Eh-pH diagram for arsenic and iron published by Ford et al. (2007). Measured pH/ORP data from these piezometers aligned along the goethite/Fe²⁺ slope, demonstrating that ORP appears to be controlled by the iron chemistry. This was observed throughout the site areas with elevated concentrations of dissolved iron.
- Historical investigations indicate that only the inorganic arsenic species [i.e., arsenite (As(III)) and arsenate As(V))] are encountered in the portion of the arsenic plume that was investigated during the pilot aeration tests. As(III) and As(V) speciation analyses that were performed prior to air sparging indicated that As(III) was dominant over As(V) in the groundwater. EPA/ORD investigations confirm that most of the arsenic extracted from the soil samples collected upgradient of and within the air sparge areas was in the As(III) form, similar to the chemical extraction and speciation testing as described in Section 2.2.2. These results indicate that prior to and after air sparging, the oxidation of As(III) to As(V) was not occurring at a significant rate.



Figure 2.8 Pre and post air sparging dissolved iron and arsenic concentrations.

2.4 Biotic Oxidation of As(III)

At the onset of this work, it was not clear whether oxidation of As(III) to As(V) during air sparging was an important process that needed to be considered when quantifying partitioning of arsenic from groundwater to soil; therefore, part of the investigation included determining the overall physiological potential for microbiological transformation of As(III) in soils and groundwater at the site. Specifically, the physiological potential toward the oxidative biotransformation of As(III) to As(V) was evaluated by a PCR-based survey targeting three relevant genes. Genes of interest that were targeted for PCR included *aioA* and *arxA*, which are involved in oxidation of As(III) to As(V), and *dsr1* which is a likely candidate for providing an electron acceptor for As(III) oxidation via dissimilatory sulfate reduction. The final report of activities conducted under this task (Task 2) are provided in Appendix C. The conclusion of this study was that organisms responsible for oxidation of As(III) to As(V) by specific physiological mechanisms are either not present or are present in extremely low concentrations. It is possible that the oxidation of As(III) may be occurring anaerobically via coupling of As(III) oxidation with SO₄ reduction.

2.5 Summary of Key Findings and Geochemical Modeling Approach

The soil and groundwater data were used to evaluate arsenic partitioning from groundwater to soil and, hence, the fate and transport of arsenic in groundwater under ambient anoxic or under air sparging aerobic conditions. Key findings include:

1) Decreases in the arsenic concentrations in groundwater coincide with decreases in iron concentrations. Iron is oxidized, precipitates, and the precipitated iron oxide removes arsenic from the groundwater. HFO forms first and over time transforms to more thermodynamically stable iron minerals (goethite and hematite). Both the chemical extraction analysis performed by EPA/ORD and the sequential extraction analysis performed by USACE ERDC-EL identified a significant portion of the solid-phase arsenic as associated with poorly crystalline iron minerals (i.e. ferrihydrite or HFO). The sequential extraction analysis performed by ERDC-EL also found that a significant portion of the solid-phase arsenic was associated with the stable residual minerals while the majority of the chemical extraction analyses performed by EPA/ORD showed that only a small portion of the arsenic was associated with more crystalline forms of iron. Therefore, there is some uncertainty in the site-specific conditions and timeframes under which HFO transforms into the more crystalline forms of iron.

It has been noted in the literature that ferrihydrite transforms to goethite and to hematite under certain conditions (Cornell and Schwertmann, 1996) and that factors affecting the rate of transformation include:

- **Temperature** Transformation of HFO to hematite has been observed at temperatures as low as 4 °C. The rate increases with increasing temperature.
- Presence of seed crystals Formation of goethite from HFO involves dissolution of HFO followed by nucleation and growth of goethite in solution. This occurs naturally, since the solubility of HFO is greater than the solubility of goethite. Goethite formation is catalyzed by the presence of seed crystals of either goethite or hematite. There is evidence that the ordered regions in HFO can also serve as sites for goethite crystallization.
- **pH** The rate of transformation of HFO increases as the pH of the system rises from 2 to 12.

- 2) As(III) is the dominant form of arsenic in groundwater and in soil. Oxidation of As(III) to As(V) in groundwater under ambient conditions does not appear to influence partitioning of arsenic from groundwater to soil, possibly because oxidation of As(III) to As(V) occurs much slower than HFO formation and arsenic partitioning to soil. It has been reported that under natural water conditions, oxidation of As(III) or reduction of As(V) occurs at a sufficiently slow rate such that water samples can be collected, transported and analyzed before excessive change in species distribution takes place (Cherry et al., 1979).
- 3) Oxidation of Fe(II) is not instantaneous at the pH range encountered in the field (4.5 to 6). This allows precipitation of iron oxides over a large volume of the aquifer and decreases the accumulation of iron oxides in the immediate vicinity of the air sparge wells.
- 4) When groundwater is exposed to the atmosphere, the pH of groundwater is influenced by both iron oxidation and precipitation (which decreases the pH) and the degassing of CO₂ from the supersaturated groundwater (which increases the pH).

PHREEQC, version 3 (Parkhurst and Appelo, 1999; Parkhurst and Appelo, 2013) was selected to model the fate and transport of arsenic under ambient and air sparge conditions. The database for PHREEQC was evaluated against the key findings to ensure that key processes were incorporated. Reactions that are slow under the site conditions such as pH-controlled reactions and microbial processes were not included in the modeling effort. PHREEQC, with the *Wateq4f* database that addressed all key processes outlined in this section, was used to calibrate the model to bench-scale data. Summary of key findings and the processes used to address them are as follows:

- Iron (Fe (II)) oxidation to HFO is not instantaneous (i.e., kinetics control the rate and extent of reaction). Rate constants for Fe(II) oxidation to HFO were added to PHREEQC to account for this phenomenon. Specifically, Dietz and Dempsey (2001) rate equations and constants that were developed and applied to oxidation of iron in acid mine drainage were added to PHREEQC.
- 2) Arsenic partitioning from groundwater to HFO: According to the literature, surface complexation models can be used to quantify sorption on variably charged surfaces such as Fe oxides (Dzombak and Morel, 1990). There are three options available in PHREEQC for modeling surface-complexation reactions: the generalized two-layer model of Dzombak and Morel (1990); a model with an explicitly calculated diffuse layer from Borkovec and Westall (1983); and, the non-electrostatic model of Davis and Kent (1990). The Dzombak and Morel diffuse-layer model accounts for the dominant anions and cations and does not account for the sorption of trace metals. This model was selected because it has been widely used by EPA and others, successfully applied to field cases, and has an extensive database. Surface complexation constants taken from Dzombak and Morel (1990) are available in the PHREEQC databases phreeqc.dat and wateq4f.dat. Wateq4f.dat was selected for the analysis since phreeqc.dat does not include arsenic.
- 3) As(III) is the dominant form of arsenic in groundwater, and As(III) in groundwater does not appear to oxidize to As(V) prior to partitioning to soil. PHREEQC will allow the oxidation or reduction of arsenic to proceed to equilibrium, with most arsenic oxidizing to As(V) in the presence of oxygen and most arsenic reduced to As(III) under anaerobic conditions regardless of the length of time it takes this process to occur. Since DO is present in the system at concentrations < 1 mg/L under ambient groundwater and > 1 mg/L under aerobic conditions, PHREEQC converts most of the

As(III) to As(V) prior to partitioning to HFO. For that reason, PHREEQC was modified to remove the oxidation of As(III) since the partitioning of As(III) to soil takes place much more quickly than the oxidation of As(III) to As(V).

4) Degassing of carbon dioxide (CO₂) is a key reaction that influences the pH of the system. The pH of the system is pertinent since both the rate of oxidation of Fe(II) and partitioning of arsenic to HFO are functions of pH. Degassing of CO₂ is incorporated in the model by allowing a given percent of CO₂ in groundwater to partition to the gas phase.

Detailed information regarding the incorporation of the above processes in the model and the use of the model to calibrate results from the bench-scale tests and the field are provided in Section 3.

2.6 Quality Control/Quality Assurance

As required by EPA's quality assurance policy, data collection efforts and modeling studies described in this report were conducted under approved Quality Assurance Projects Plans (QAPPs) and followed standard quality control (QC) procedures. Sampling conducted by the USACE was completed following procedures in the Department of Defense (DoD) Environmental Field Sampling Handbook, Revision 1.0 (April 2013). Work conducted by the USACE ERDC-EL was performed following standard method QC procedures, including, but not limited to: blanks, blank spikes, duplicates, and matrix spikes. Instruments were calibrated using NIST-traceable, commercially available standards with second source NIST-traceable calibration verification standards. Recovery ranges for all QC samples followed method guidance (e.g. 10% for ICV and CCV recoveries, 20% for BS and MS recoveries). Internal standards were added in-line for all ICP-AES (e.g. Scandium and Yttrium) and ICP-MS (e.g. Germanium, Rhodium, Terbium, and Bismuth) analyses to correct for instrumental drift, and palladium-magnesium or nickel nitrate matrix modifiers were used for all GF-AAS analyses. Laboratory characterization studies conducted by EPA's Office of Research and Development were conducted under the QAPP titled "Monitored Natural Attenuation of Metals" (G-GWERD-0014907-QP-1-5). Data qualifiers were applied as appropriate and are noted in the tabulated data.



SECTION 3 Bench Scale Tests

3.1 Background

Laboratory tests were conducted at the Vineland Chemical Company Superfund Site in order to investigate sorption of arsenic onto iron oxides in native soil and when freshly precipitated from groundwater. Data collected from the laboratory tests were used to determine if published thermodynamic constants were adequate in describing the arsenic partitioning between groundwater and iron oxides in the site soil as well as iron oxides that precipitate from the groundwater. Additionally, laboratory test data were used to calibrate the model to describe the rate of iron oxidation using a rate equation that incorporates both heterogeneous and homogeneous oxidation.

Iron and arsenic concentration data were collected prior to and during the air sparging pilot test. The data were used to verify that the fate and transport mechanisms identified during model calibration were consistent with the field observations.

Three types of bench-scale tests were performed in the lab following EPA (1992) guidance for batch-type procedures for estimating soil adsorption of chemicals when relevant. These tests include:

- 1. Time to Equilibrium Test Groundwater was mixed with soil and the concentration of arsenic and iron were monitored for a period up to 24 hours to determine the time it takes the system to come into equilibrium.
- 2. Sorption/Reaction Test Groundwater was mixed with soil at different ratios to determine the impact of soil quantity on arsenic sorption.
- **3. Column Test** Groundwater was passed through a column filled with soil to simulate groundwater flow in the aquifer.

Each test was performed on two types of soil. The soils that were used in the lab tests had low levels of arsenic (< 10 mg/kg), but each soil type had a different iron content so that the role of the native iron in soil in immobilizing arsenic could be assessed. Table 3.1 lists the arsenic and iron content of each soil.

Table 3.1 Soils used in batch and column tests											
Soil Type	Sample Interval (ft bgs)	Arsenic (mg/kg)	Iron (mg/kg)								
Sand	20 - 25	3.06 - 5.34	634 - 1,950								
Red/Orange Sand	35 - 36.5	3.97 - 9.52	9,200 - 10,300								

Both types of soil were collected from the site by sonic drilling at location MP-1 as shown on Figure 3.1. The soil was collected prior to any air sparging activities on the site, so the subsurface in this region was anoxic at the time of soil collection. The soil was immediately transported (<24 h) to an on-site lab in acetate sleeves. Soil at the edges of the sleeves was removed and the soil was placed into an anaerobic chamber. These actions were performed shortly after collection to minimize oxidation of the iron in the soil. All batch tests were assembled and sealed inside the anaerobic chamber. Due to space limitations, the batch test bottles were then rotated on a tumbler outside of the anaerobic chamber. Batch test bottles were transferred back inside the anaerobic chamber before they were unsealed for sampling. All bottles were covered with foil for the duration of the tests to minimize exposure to light. Column tests were conducted entirely inside the anaerobic chamber. Groundwater that was used in the lab tests was collected from MW75S, shown on Figure 3.1 using standard low flow sampling methods. Groundwater in this location is anoxic, iron rich, impacted by arsenic, and generally had a pH between 5.20 and 6.12 and an ORP between -6 and 74 upon sampling.



Figure 3.1 Soil and groundwater collection locations.

3.2 Laboratory Tests and Results

The following sections provide a description of each laboratory test and a brief discussion of the analytical results from the test.

3.2.1 Time to Equilibrium Tests

Time to equilibrium tests were conducted by filling four bottles with approximately 550 mL of groundwater and 100 g soil. Another four bottles were filled with about 550 mL groundwater and no soil to serve as the "groundwater control" so that changes in concentrations due to soil could be differentiated from those occurring in groundwater under ambient laboratory conditions. All eight bottles were placed in a rotary agitator and sampled after different contact times.

Four separate sets of Time to Equilibrium batch tests were conducted. The first set included sand with a lower iron content. The second set included red/orange sand with a higher iron content. The third and fourth sets of batch tests replicated the first two sets except that the pH of the groundwater was adjusted to 4 using H_2SO_4 before being introduced into the batch tests. The results of all four sets of batch tests are listed in Table 3.2 and shown on Figure 3.2.

In batch tests that included soil, the majority of the observed decrease in dissolved arsenic occurred within the first one to two hours of the test. Arsenic concentrations continued to decrease after two hours, but the rate slowed. Dissolved iron was also monitored throughout the 24-hour test period (Figure 3.3). A period of 24 hours was deemed sufficient for the subsequent sorption/reaction tests.

Some iron precipitated out of the groundwater control tests and resulted in a decrease in dissolved arsenic. The decrease in arsenic in the groundwater control tests was always less than in the tests involving soil. In some tests, the dissolved iron concentration increased when soil was added, but these results did not impact the decision to continue with a 24-hr testing time. An increase in dissolved iron concentration was also observed in some of the sorption/reaction batch tests and column tests involving soil. The batch and column tests did not directly demonstrate the mechanism responsible for the increase in dissolved iron, so it was assumed that either a release of adsorbed ferrous iron or a dissolution of an iron mineral in the soil had taken place.

Table 3.2 Tin	ne to equili	brium tes	st results							
Description	Date	Contact Time	MW75S Groundwater	Soil (g)	Aque Concen (mg	eous itration g/L)	Measured in the lab			
		(hr)	(mL)		As (Diss)	Fe (Diss)	рН	ORP (mV)	Temp (°F)	
	9/8/2015	0	N/A-Initial C	Condition	2.19	10.5	5.78	94		
	9/8/2015	2	550	100	1.5	7.8	5.8	-51	68.2	
	9/8/2015	4	550	100	1.44	8.12	5.78	-34	69.1	
a.) Time To	9/8/2015	6	550	100	1.33	7.55	5.69	-16	71	
Equilibrium,	9/9/2015	24	550	100	0.965	4.89	5.9	1	70.6	
adjustment	9/8/2015	2	550	0	2.12	10.4	5.85	-35	68	
	9/8/2015	4	550	0	2.07	10.3	5.6	-17	70.1	
	9/8/2015	6	550	0	1.83	10.2	5.69	-26	73.6	
	9/9/2015	24	550	0	1.48	8.58	5.93	-13	73.1	
	11/12/2015	0	N/A-Initial C	Condition	1.39	7.81	5.70	98	64.5	
	11/12/2015	1	550	0	1.37	7.7	5.65	93	67.8	
h) Time To	11/12/2015	1	550	100	0.545	9.28	5.78	70	67.8	
Equilibrium, 1 Red/orange 1 sand, no pH 1 adjustment 1	11/12/2015	3	550	0	1.34	7.7	5.68	89	72.1	
	11/12/2015	3	550	100	0.432	10.3	5.74	23	71.4	
	11/12/2015	5	550	0	1.37	7.82	5.70	61	75.8	
	11/12/2015	5	550	100	0.277	8.63	5.63	55	74.9	
	11/13/2015	24	550	0	1.02	5.63	5.53	50	76.8	
	11/13/2015	24	550	100	0.143	7.9	5.59	-5	75.6	
	12/8/2015	0	N/A-Initial Condition		1.87	9.08	3.96	260	64.5	
	12/8/2015	1	550	0	1.89	9.16	3.99	176	68.1	
	12/8/2015	1	550	100	1.58	10.5	5.19	-21	69.2	
c.) Time To	12/8/2015	3	550	0	1.75	9.1	3.94	179	79.7	
Equilibrium,	12/8/2015	3	550	100	1.56	11.1	5.32	33	71.5	
sand, pH=4	12/8/2015	5	550	0	1.9	9.21	3.95	153	77	
	12/8/2015	5	550	100	1.51	10.2	5.38	40	76.4	
	12/9/2015	24	550	0	1.76	8.2	3.86	297	74.5	
	12/9/2015	24	550	100	1.41	11	5.48	93	73.9	
	11/17/2015	0	N/A-Initial C	Condition	1.76	9.4	4.00	268	62.5	
	11/17/2015	1	550	0	1.74	9.34	4.01	249	67.3	
	11/17/2015	1	550	100	0.76	12.5	5.15	11	67	
d.) Time To	11/17/2015	3	550	0	1.77	9.35	4.02	260	70.8	
Equilibrium,	11/17/2015	3	550	100	0.586	14.9	5.43	-55	71.3	
sand. pH=4	11/17/2015	5	550	0	1.77	9.44	4.03	254	74.3	
, p	11/17/2015	5	550	100	0.484	14.2	5.37	-30	74.3	
	11/18/2015	24	550	0	1.69	8.86	3.99	344	79.7	
	11/18/2015	24	550	100	0.169	14.8	5.50	29	79.7	



Figure 3.2 Time to equilibrium batch test results: Dissolved arsenic vs. time.



Figure 3.3 Time to equilibrium batch test results: Dissolved iron vs. time.

3.2.2 Sorption/Reaction Tests

Four separate sets of sorption/reaction batch tests were conducted:

- 1) Sand (low iron content) and groundwater were mixed at different ratios. No pH adjustment was made.
- 2) Red/orange sand (high iron content) and groundwater were mixed at different ratios. No pH adjustment was made.
- 3) Sand and groundwater were mixed at similar ratios. pH was varied by adding H_2SO_4 or NaOH.
- 4) Red/orange sand and groundwater were mixed at similar ratios. pH was varied by adding H_2SO_4 or NaOH.

In each set of batch tests, bottles containing groundwater or soil plus groundwater were assembled and sealed inside the anaerobic chamber. The bottles were rotated on a tumbler for 24 hours before being transferred back into the anaerobic chamber, unsealed, and sampled. The results of all four tests were used for model calibration (discussed in Section 3.3 below).

TEST 1: Sand (low iron content) and groundwater mixed at different ratios. No pH adjustment.

Seven bottles were filled with different ratios of sand and groundwater to evaluate the effect of soil/ water ratios on the sorption of arsenic. Soil amounts ranged from 30 g to 470 g. One bottle was also filled only with groundwater to serve as a control. The details and results of each test are listed in Table 3.3. Plots of the results are shown on Figure 3.4. As the ratio of soil to water increased, the concentration of arsenic in groundwater decreased. Batch tests in which more arsenic was removed also corresponded to tests where more iron precipitated out of solution. The controls also experienced a decrease in arsenic and iron, suggesting that freshly precipitated iron contributed to arsenic sorption. This hypothesis was explored in more detail with geochemical modeling and is discussed in Section 3.3 below.

TEST 2: Red/orange sand (high iron content) and groundwater were mixed at different ratios. No pH adjustment.

This set of batch tests was conducted in a similar way to Test 1 above, except the sand used in Test 2 was higher in iron than the sand used in Test 1. Six bottles were filled with differing ratios of soil and groundwater, and one bottle was filled with only groundwater to serve as the control. Soil amounts ranged from 30 g to 400 g. The results of this set of batch tests are shown on Figure 3.5 and listed in Table 3.4. In general, as the ratio of soil to groundwater was increased, so did the rate and efficiency of arsenic removal. Almost all of the arsenic in solution was removed with the highest ratio of soil to groundwater that was tested.

Dissolved iron concentrations were also plotted on Figure 3.5. The iron concentration decreased in batch tests involving low amounts of soil but increased above the initial measured value in several of the batch tests with higher amounts of soil and this behavior was considered to be a result of either iron desorption or dissolution.

TEST 3: Sand and groundwater mixed at similar ratios. pH was varied.

In this set of batch tests, six bottles were filled with groundwater and 70 g of soil. One bottle was filled with only groundwater to serve as the control. H₂SO₄ or NaOH was added to five of the six bottles containing soil to adjust the pH to a range between 4.0 and 6.8 which spans the pH values typically expected to be encountered in the field. The pH of the remaining bottle with soil and groundwater was not adjusted. Details of how much soil, groundwater, and acid or base was added to each batch test are shown in Table 3.5, which also includes the batch test results. Final dissolved arsenic, dissolved iron, As(III) and As(V) concentrations are plotted against pH in Figure 3.6. In general, more arsenic and iron remained in solution at lower pH values.

A decrease in arsenic was observed at all pH values. However, at pH values below 5, iron concentrations were higher than initially measured, suggesting either release of adsorbed ferrous iron or dissolution of iron minerals in the soil.

TEST 4: Red/orange sand and groundwater mixed at similar ratios. pH was varied.

This set of batch tests was conducted in much the same way as Test 3 above, except the sand used in these batch tests had a higher iron content than the sand used in Test 3. Six bottles were filled with groundwater and 70 g of soil. One bottle was filled with only groundwater to serve as the control. H_2SO_4 or NaOH was added to five of the six bottles containing soil to adjust the pH to a range between 5.0 and 6.3 which covers the range of pH values expected to occur in the field under normal conditions. The pH of the remaining bottle with soil and groundwater was not adjusted. Details of how much soil, groundwater, and acid or base were added to each batch test are shown in Table 3.6 along with the results of each test.

Final dissolved arsenic, dissolved iron, As(III) and As(V) concentrations are plotted against pH in Figure 3.7. As the pH decreased, more arsenic and iron generally remained in solution, but the pattern is much less distinct than was observed in Test 3. All of the batch tests in which the pH was decreased showed an increase in dissolved iron concentration above the initially measured value.

Table 3.3 Sorption/reaction batch test results using sand with a low iron content												
		MW/755		Aqueo	ous Conce	entration	Measured in the lab					
Description	Date	Groundwater (mL)	Soil (g)	As (Diss)	Fe (Diss)	As (Total)	Fe (Total)	рН	ORP (mV)	Temp (°F)	Alkalinity (mg/L as CaCO₃)	
	10/1/2015	N/A-Initial Cor	ndition	2.04	10.5	2.24	11.3	5.53	36	62.8	20	
	10/1/2015	575	0	1.73	9.26	2.18	11	5.56	14	72.7		
1)	10/1/2015	550	33.25	1.36	5.5	N/A	N/A	5.51	58	72	15	
Sorption/	10/1/2015	550	66.5	1.18	4.32	N/A	N/A	5.43	57	72		
Reaction,	10/1/2015	500	133	1.04	3.64	N/A	N/A	5.58	39	72	15	
sand, no pH	10/1/2015	450	266	0.962	4.17	N/A	N/A	5.7	-39	71.8		
adjustment	10/1/2015	400	332.5	0.803	3.55	N/A	N/A	5.83	-37	71.7		
	10/1/2015	350	339	0.765	3.32	N/A	N/A	5.88	-200	71.9	20	
	10/1/2015	300	465.5	0.638	3.28	N/A	N/A	5.77	-239	70.7		

Table 3.4 Sorption/reaction batch test results using sand with a high iron content														
		MW75S	Soil (g)		Aqueous Concentration (mg/L) Measured in the la									
Description	Date	Groundwater (mL)		As (Diss)	Fe (Diss)	As (Total)	Fe (Total)	As (III)	As (V)	рН	ORP (mV)	Temp (°F)		
2.)	12/3/2015	N/A-Initial Condition		1.832	9.247	2.147	10.52	1.462	0.28	5.66	24	64.3		
	12/3/2015	575	0	1.422	6.896	N/A	N/A	1.212	0.135	5.58	-13	68.4		
Sorption/	12/3/2015	550	33.25	0.428	6.283	N/A	N/A	0.392	0.0428	5.5	23	69.7		
Reaction,	12/3/2015	550	67.5	0.267	5.855	N/A	N/A	0.234	0.0262	5.46	21	70.2		
Red/orange sand, no pH adjustment	12/3/2015	500	133	0.118	9.379	N/A	N/A	0.103	0.0113	5.64	-97	67.1		
	12/3/2015	450	266	0.054	11.5	N/A	N/A	0.042	0.0046	5.47	-67	70.5		
	12/3/2015	350	399	0.03	13.81	N/A	N/A	0.0262	0.0033	5.51	-98	71.2		

Table 3.5 Sorption/reaction batch test results using sand with a low iron content and pH adjustment														
	Date	MW75S Groundwater (mL)	Soil (g)	H₂SO₄ (mL)	NaOH (mL)	Aqueous Concentration (mg/L) Measured in the								the lab
Description						As (Diss)	Fe (Diss)	As (Total)	Fe (Total)	As (III)	As (V)	рН	ORP (mV)	Temp (°F)
	3/31/2016	N/A-Initial Condition				2.05	10	2.51	12.2	1.55	0.181	5.7	54	57.9
	4/1/2016	552	0	0	0	1.41	6	N/A	N/A	1.17	0.11	5.68	77	71.3
3.)	4/1/2016	517	67.5	0	0	1.34	6.34	N/A	N/A	1.08	0.107	5.81	23	71.4
Sorption/	4/1/2016	505	67.5	10	0	1.43	8.77	N/A	N/A	1.16	0.11	5.38	99	72
Reaction,	4/1/2016	503	67.5	20	0	1.56	13.7	N/A	N/A	1.26	0.146	4.73	153	71.5
sand, variable pH	4/1/2016	492	67.5	30	0	1.61	15.2	N/A	N/A	1.3	0.147	4.41	173	72
	4/1/2016	487	67.5	40	0	1.64	15.2	N/A	N/A	1.26	0.176	4.19	200	72.5
	4/1/2016	475	67.5	50	0	1.65	17.9	N/A	N/A	1.3	0.145	4.01	234	70.6
	4/1/2016	515	67.5	0	5	1.33	2.65	N/A	N/A	0.891	0.269	6.83	-117	71.1

Table 3.6 Sorption/reaction batch test results using sand with a high iron content and pH adjustment														
	Date	MW75S Groundwater (mL)	Soil (g)	H₂SO₄ (mL)	NaOH (mL)	Aqueous Concentration (mg/L) Measured in the							the lab	
Description						As (Diss)	Fe (Diss)	As (Total)	Fe (Total)	As (III)	As (V)	рН	ORP (mV)	Temp (°F)
	3/23/2016	N/A-Initial Co		ondition		1.54	7.81	2.54	12.1	1.28	0.138	6.01	35	66
4)	3/24/2016	550	0	0	0	0.896	3.14	N/A	N/A	0.758	0.08	5.57	109	65.2
4.) Sorption/	3/24/2016	508	67.5	0	0	0.176	15.9	N/A	N/A	0.149	0.018	5.92	-93	64.7
Reaction,	3/24/2016	507	67.5	5	0	0.256	18.5	N/A	N/A	0.217	0.024	5.84	-94	65.6
Red/orange sand, variable pH	3/24/2016	505	67.5	10	0	0.24	21.4	N/A	N/A	0.208	0.026	5.89	-53	65.3
	3/24/2016	498	67.5	20	0	0.284	22.6	N/A	N/A	0.249	0.028	5.45	82	66
	3/24/2016	481	67.5	30	0	0.26	28.3	N/A	N/A	0.224	0.03	5.00	104	62.4
	3/24/2016	515	67.5	0	4	0.179	1.4	N/A	N/A	0.159	0.019	6.27	-123	62.9



Figure 3.4 Sorption/reaction batch test results: Sand mixed with groundwater without pH adjustment.



Batch Test Description:

- · Six bottles were filled with red/orange sand and groundwater, one bottle was filled with only groundwater to serve as a control. Soil amounts were varied from approximately 30g to 400g.
- · Bottles were sampled after 24 hours of mixing on a rotary tumbler.

Initial Concentrations

- Red/Orange Sand from MP-1 (35-36.5' bgs) As = 5.88 mg/kgFe = 10,300 mg/kg
- Groundwater: MW75S As = 1.83 mg/L (Dissolved) Fe = 9.25 mg/L (Dissolved)

Figure 3.5 Sorption/reaction batch test results: Red/orange sand mixed with groundwater without pH adjustment.



Figure 3.6 Sorption/reaction batch test results: Sand mixed with groundwater with pH adjustment.



Figure 3.7 Sorption/reaction batch test results: Red/orange sand mixed with groundwater with pH adjustment.

3.2.3 Column Test

Arsenic-impacted groundwater from MW75S was run through a set of three columns: one column packed with sand, one column packed with red/orange sand, and one column packed with "Filpro" sand composed of at least 99% silicon dioxide which served as a control. These columns are shown in Figure 3.8. The first sand has a low iron concentration (approximately 1,000-2,000 mg/kg iron) while the concentration of iron in the red/orange sand is much higher (about 9,000-10,000 mg/kg iron). These are the same soil types that were used in the batch tests. Groundwater was pumped at approximately 4 mL/min from the bottom of each column to the top of each column where one pore volume (about 118 mL) was allowed to accumulate above the packing material before removal. At this flow rate, one pore volume took approximately 30 minutes to flush through the column and another 30 minutes to accumulate above the packing material before volumes were completely flushed through the column with the tenth filling the column, but not completely flushed through. Pore volumes 1, 3, 5, 7, and 9 from each column were sampled for dissolved arsenic, iron, As(III), and As(V). Analytical sample results are presented in Table 3.7.

A single container was used to provide groundwater for all three column tests, which were run concurrently. Several samples were collected from this container throughout the tests so that the influent concentrations of arsenic and iron could be tracked. Figure 3.9a shows the influent concentrations of arsenic and iron through time. Note that dissolved iron is plotted on the secondary y-axis, and both arsenic and iron follow the same decreasing trend. Figure 3.9 also shows the column effluent arsenic (Figure 3.9b) and iron (Figure 3.9c) concentrations through time as well as the influent concentration corresponding to each sampled pore volume. Columns 1 and 3 approached arsenic breakthrough while arsenic concentrations in the effluent of column 2 remained rather low throughout the entire test.

Dissolution or desorption of iron in column 2 (sand with the high iron content) was observed in the sample of the first pore volume to be flushed through the column. Figure 3.9c shows that the first sample resulted in a higher concentration of dissolved iron in the effluent than was measured in the influent suggesting that some of the iron in the sand had gone into solution under the conditions created in the lab. The iron concentration observed in the effluent of column 2 then decreased as additional pore volumes were flushed through the column.

An increasing trend in the iron concentration of the effluent was observed in columns 1 and 3 (Figure 3.9c). Iron concentrations in the first pore volume flushed through these columns were very low and subsequently increased as more pore volumes were flushed through the columns. This suggests that dissolution of the iron minerals was not occurring or was only minimally occurring.

Sample results of As(III) and As(V) concentrations are plotted on Figure 3.10. As(III) is plotted on the primary y-axis, and As(V) is plotted on the secondary y-axis. The concentrations of As(III) and As(V) in the column influent followed the same decreasing trend with time. Effluent concentrations in column 1 and column 3 increased to concentrations approximating the influent. Effluent concentrations remained low (<0.01 mg/L total arsenic) in the high-iron column (column 2). Concentrations of As(III) remained higher than As(V) throughout the column tests.



(Fe = 1,000-2,000 mg/kg)

Column 2: Sand with high iron (Fe = 9,000-10,000 mg/kg)

Figure 3.8 Column tests.

Table 3.7 Column test analytical results													
Column	Pore Volume	Time Collected	As (mg/L)	Fe (mg/L)	As (III) (mg/L)	As (V) (mg/L)	Cl ⁻ (mg/L)	N ³⁻ (mg/L)	SO ₄ ²⁻ (mg/L)	Mg²+ (mg/L)	K⁺ (mg/L)	Na⁺ (mg/L)	Ca ²⁺ (mg/L)
Influent	1	8/24/2016 8:00	2.16	10.4	2.098	0.29	2.31	0.0264	8.73	0.306	1.35	2.31	1.48
Influent	3	8/24/2016 10:00	2	9.66	2.065	0.266							
Influent	5	8/24/2016 11:30	1.91	9.42	2.024	0.265							
Influent	7	8/24/2016 12:34	1.93	9.26	1.996	0.265							
Influent	9	8/24/2016 13:45	1.9	9.17	1.976	0.252							
Influent	10	8/24/2016 15:20	1.92	9.18	1.973	0.227							
1	1	8/24/2016 10:15	0.393	0.437	0.431	0.0488							
1	3	8/24/2016 11:35	0.987	0.225	1.059	0.1							
1	5	8/24/2016 12:40	1.67	1.97	1.743	0.159							
1	7	8/24/2016 14:00	1.8	6.28	1.83	0.201							
1	9	8/24/2016 15:29	1.75	9.08	1.798	0.176				0.62	1.42	2.67	2.61
2	1	8/24/2016 10:40	0.204	13.5	0.0019	0.0006							
2	3	8/24/2016 11:43	0.387	5.99	0.0042	0.001							
2	5	8/24/2016 12:44	0.257	6.05	0.0027	0.0007							
2	7	8/24/2016 14:05	0.0026	4.64	0.0025	0.0009							
2	8	8/24/2016 14:54					2.34	0.0514	8.85				
2	9	8/24/2016 15:36	0.337	3.77	0.0031	0.0007				0.428	1.37	2.71	1.38
3	1	8/24/2016 10:45	1.35	0.255	1.4	0.112							
3	3	8/24/2016 12:08	1.76	2.3	1.897	0.168							
3	5	8/24/2016 13:15	1.86	4.91	1.955	0.205							
3	7	8/24/2016 14:40	1.79	5.83	1.91	0.201							
3	8	8/24/2016 15:15					2.33	0.348	16.3				
3	9	8/24/2016 15:41	1.89	6.6	1.881	0.18				0.51	1.46	2.81	1.78

Column 1 = Sand

Column 2 = Red/orange Sand Column 3 = "Filpro" 99% Silica Sand



Figure 3.9 Column tests results: Influent and effluent arsenic and iron concentrations.



Y-axis magnitude varies by plot

Figure 3.10 Column tests results: Influent and effluent arsenic speciation.

The pH, ORP, and temperature of the influent and effluent were measured frequently throughout the test. These values are shown in Table 3.8 and plotted with time in Figure 3.11. It is likely that degassing of CO_2 during sample collection influenced the measured pH in most of the tests, especially in the samples collected from the effluent. There are no clear trends in pH or ORP associated with the column effluent samples. The pH of the influent appears to gradually increase throughout the duration of the test while the ORP decreases, which is consistent with the slow degassing of CO_2 .

Table 3.8 Column test laboratory measured parameters										
Column	Pore Volume	Time Collected	рН	ORP (mV)	Temp (°F)					
Influent	1	8:00:00 AM	5.8	40	67.8					
Influent	3	10:00:00 AM	5.97	14	67.9					
Influent	5	12:34:00 PM	6.08	-32	68.8					
Influent	7	1:45:00 PM	6.17	-28	67.8					
Influent	9	3:20:00 PM	6.22	-26	68					
1	1	10:15:00 AM	6.35	71	69.1					
1	2	10:52:00 AM	6.46	-44	69.2					
1	3	11:35:00 AM	6.34	-5	69.2					
1	4	12:05:00 PM	6.19		69					
1	8	3:00:00 PM	6.09	-71	68.5					
1	9	3:29:00 PM	6.31	-68	68.4					
2	1	10:40:00 AM	5.61	72	68.2					
2	3	11:43:00 AM	5.84	73	69.1					
2	4	12:14:00 PM	6.2	63	68.8					
2	8	2:45:00 PM	5.63	60	68.8					
2	9	3:36:00 PM	6.03	56	68.5					
3	1	10:45:00 AM	6.4	-10	68.3					
3	3	12:08:00 PM	6.6		69.3					
3	4	12:51:00 PM	6.24	-37	69					
3	8	3:15:00 PM	6.19	-35	68.9					
3	9	3:41:00 PM	6.22	-39	68.6					



The pH and ORP of the influent and effluent were monitored throughout the column test. The plots to the left show the variation in these parameters throughout the test. Degassing of CO2 was likely to have occurred and could have influenced pH measurements.

Column 1 = Low Fe Sand (1,000-2,000 mg/kg Fe) Column 2 = High Fe Red/Orange Sand (9,000-10,000 mg/kg Fe) Column 3 = "Control"

Figure 3.11 Column tests results: Parameters measured in the laboratory.

3.3 Model Simulations

The geochemical model PHREEQC, version 3 (Parkhurst and Appelo, 1999; Parkhurst and Appelo, 2013) was used to simulate arsenic sorption and iron precipitation under laboratory and field conditions. Model calibration involved identifying key parameters impacting the fate and transport of arsenic and iron in the sorption/reaction batch tests and column tests, and adjusting those parameters until the modeled arsenic and iron concentrations came close to the concentrations measured in the lab. The calibration process resulted in a range of values for fate and transport parameters that could be used to predict arsenic and iron concentrations in the field.

3.3.1 Model Calibration to Batch and Column Test Data

The default parameter values found in the *wateq4f* database that accompanies PHREEQC were used in the model simulations. Any modifications made to the *wateq4f* database are discussed in 2.5 and are shown in Appendix D. A summary of the conditions and assumptions applied during model calibration is given below:

- The oxidation of As(III) to As(V) or reduction of As(V) to As(III) occurs slowly under laboratory and field conditions and is not significant over the course of the batch tests or column tests. Therefore, these processes were not allowed to occur in the model.
- 2) All processes were assumed to proceed to equilibrium with the exception of iron oxidation. Both homogeneous and heterogeneous oxidation mechanisms contribute to the rate of iron oxidation. The kinetics of iron oxidation were described in the model using the following equation:

$$rate = -k_{hom}[Fe(II)][O_2][H^+]^{-2} - k_{het}[Fe(III)][Fe(II)][O_2][H^+]^{-1}$$

The homogeneous (k_{hom}) and heterogeneous (k_{het}) rate constants (8.4E-14 mol/L/sec and 9.5E-04 L/mol/sec, respectively) were taken from Dietz and Dempsey (2001) and corrected for temperature as needed using the Arrhenius equation. The initial solid Fe(III) included in the rate calculations was assumed to be equal to the difference between total and dissolved iron initially measured in the groundwater and a small percentage of the iron in the soil (0.2%). Initial oxygen was assumed to be less than 1 mg/L in the majority of the simulations.

- 3) Arsenic sorption was modeled using surface complexation and the parameters for HFO from Dzombak and Morel (1990). These include a specific surface area of 600 m²/g and a weak site density of 0.2 moles per mole of iron. Sorption of arsenic to HFO was assumed to be instantaneous.
- 4) Iron that precipitated out of solution over the course of the batch or column tests was considered to be HFO and available as a sorption surface for arsenic. In laboratory batch tests involving soil, a small percentage of iron in soil, ranging from 0.5% to 5%, was also assumed to be HFO and available as a sorption surface in order to obtain a good calibration. The percentage of iron in soil assumed to be HFO was even smaller in the column tests and was at most 0.1%. The higher sorption capacity in the batch tests could be due to suspension of the HFO compared to precipitation on existing surfaces during the column tests.

- 5) Degassing of CO₂ results in an increase in pH. In most instances, the amount of CO₂ degassing allowed in the model ranged from approximately 10% to 65% of the initial concentration. There were several instances where up to 92% degassing was allowed in order to match pH and iron concentrations that were observed during the column tests.
- 6) As noted above, the final measured iron concentration was often higher than the initial concentration in batch tests that included soil. This phenomenon could potentially be due to either dissolution of iron minerals or desorption of ferrous iron. For modeling purposes, it was assumed that dissolution of iron was taking place, and equilibrium with magnetite and siderite was included in the model in order to simulate iron dissolution. It is possible that these minerals exist naturally or were formed under the anaerobic conditions inside the chamber where the soil was stored. Up to 5% of the iron in soil was modeled as siderite.

As noted above, the model was calibrated to match the dissolved iron and arsenic results from the batch tests. Figure 3.12 shows the overall fit of the model to the measured results for all sets of sorption/ reaction batch tests (described in Section 3.2.2). The diagonal solid black line represents a perfect match between modeled and measured concentrations. Points that fall close to the black line correspond to batch tests where the modeled results were in good agreement with the measured results. Most points fall close to this line with the exception of one noticeable outlier on the plot of modeled vs. measured arsenic. This point represents the result from the batch test conducted with low iron sand and pH adjustment with NaOH to a final pH of 6.83 where the model significantly over-predicted the amount of sorption that occurs. This discrepancy between modeled and measured results is due to removing the process of As(III) oxidation to As(V) in the model. The measured As(V) at the end of the batch test was higher than it was at the beginning of the batch test suggesting that, at this pH value, some conversion of As(III) to As(V) did take place during the test. If more arsenic was modeled in the As(V) phase, less sorption would occur because the sorption of As(III) is more favorable than the sorption of As(V) at this pH, and the model predictions would be closer to the experimental observations. These observations are consistent with the findings reported in Jang and Dempsey (2008).

Figure 3.12 also compares modeled to measured percent changes in arsenic and iron concentrations from the batch tests. It can be seen from these plots that either large or small changes in dissolved arsenic and iron concentrations could be replicated with the model.



Figure 3.12 Sorption/reaction batch tests results: Comparison of modeled to measured iron and arsenic concentrations.

The model could also replicate the majority of the dissolved iron and arsenic concentrations that were measured during the column tests (Figure 3.13) by using the modeling conditions and assumptions that are listed above. Each sampled pore volume that passed through the column was modeled separately. Approximately one hour elapsed from the time the groundwater entered each column to the time when the pore volume was removed from the column for sampling. Only the column test data from columns filled with site soil were modeled; the control column was not modeled.

Measured iron and arsenic concentrations in the effluent of the columns could generally be explained by using model parameters within a reasonable range of those used to model the batch tests, but some results were more difficult to replicate with the original model parameters. The column filled with lowiron sand experienced very rapid precipitation of iron in the groundwater followed by a gradual increase until the effluent concentrations of dissolved iron were almost the same as the influent concentrations. The initial rapid drop in iron could only be replicated by assuming an initial oxygen concentration of 2 mg/L, which is higher than the 0.2 mg/L - 0.8 mg/L assumed during model calibration to batch test results, and significant degassing of CO_2 (> 90%, also much greater than was used to model the batch tests) in order to push the pH higher and speed up the rate of iron oxidation. Additionally, sorption of arsenic was over-estimated when applying the same assumptions for calculating HFO that were used during model calibration. In order to match arsenic results from most of the column tests, HFO was assumed to be less than the amount of iron that precipitated out of solution. These observations suggest that some aspects of the fate and transport processes were poorly modeled when solid iron concentration was low and for the early pore volumes. The time scale in the field is closer to the later parts of the column tests and the batch tests (or longer), both of which were modeled using a reasonable set of parameters.

The results of the column test using sand with the higher iron concentrations were better fit using parameters within the ranges applied when modeling the batch tests. The degassing of CO_2 ranged between 10% and 60% of the initial concentration in order to match the effluent pH. The initial DO concentration was set between 0.83 mg/L and 0.88 mg/L. Arsenic concentrations could be replicated by assuming all freshly precipitated iron and between 0.02% and 0.1% of the iron in the soil was HFO, a value that was less than was assumed for the batch tests. This assumption is reasonable considering the batch tests were thoroughly mixed, exposing more of the HFO surface area. HFO precipitated on existing surfaces in the column tests and the specific surface area (area per mass) is expected to be lower.

Model results and assumptions for the batch and column tests have been tabulated in Appendix E.



Notes:

Column 1 = Low Fe Sand (1,000-2,000 mg/kg Fe) Column 2 = High Fe Red/Orange Sand (9,000-10,000 mg/kg Fe)

Colored circles on the graphs represent model calculated values. Empty circles represent measured values.

The pore volume number corresponding to the plotted data is posted next to each data point.

Figure 3.13 Column tests: Comparison of modeled and measured results.

3.3.2 Model Simulations of Field Conditions

Arsenic and iron concentrations were modeled under pre-air sparge and air sparge conditions using the methodology that was developed from the batch and column test results. The model of pre-air sparge conditions involved replicating the decrease in arsenic and iron observed between MP-9L and PZ-15 (see Figure 3.14 for well locations). These wells are spaced approximately 165 ft apart. At an average groundwater flow velocity of 2.5 ft/day, it takes approximately 66 days for groundwater to travel from MP-9L to PZ-15. Prior to air sparging, the concentrations of dissolved arsenic and dissolved iron at MP-9L were 0.989 mg/L and 11.7 mg/L, respectively. By the time groundwater had reached PZ-15, the concentration of arsenic had dropped to about 0.01 mg/L and iron had dropped to about 0.06 mg/L. The decline in dissolved iron was replicated by the model based on an initial pH of 5.8 and a DO concentration of 0.1 mg/L, both of which are consistent with measured pre-sparge field conditions. Degassing of CO₂ was not included in this model simulation because it is unlikely to occur in the field under non-air sparging conditions. After 66 days, the model was used to calculate an iron concentration of 0.044 mg/L, which is a good approximation considering there is some uncertainty in the exact pH, DO, and travel time from MP-9L to PZ-15. Figure 3.14 shows a plot of the modeled dissolved iron concentration through time. Dissolved arsenic was calculated by the model to be 0.02 mg/L (only 0.01 mg/L higher than the observed concentration) assuming that all the iron which precipitated out of solution along with less than 1% of the iron in soil is the HFO sorption surface. With these assumptions, the model predicted that 75% of the arsenic removed from groundwater was due to sorption to the freshly precipitated HFO. The remaining 25% of the arsenic removed from solution was due to sorption with iron oxides that previously were in the soil.

PHREEQC was also used to replicate the decrease in arsenic and iron that occurs between MP-1L and locations that are downgradient from the air sparge system. The goal of this simulation was to capture the general behavior of dissolved arsenic and iron as groundwater moves through the air sparged area. MP-1L is upgradient of the air sparge system and is not impacted by the air sparging, but there was some variation in iron and arsenic concentrations measured during the pilot study at this location. Dissolved iron concentrations ranged from 14.8 mg/L to 18.9 mg/L, and dissolved arsenic concentrations ranged from 1.31 mg/L to 1.87 mg/L. To reflect this variation in influent concentrations to the air sparged area, average values of dissolved arsenic and dissolved iron (1.4 mg/L and 15.5 mg/L, respectively) were used as the initial concentrations in the model.

Although concentrations downgradient of the air sparge system varied as the operational conditions of the system were changed as part of the pilot test, concentrations and field parameters measured at MP-4L serve as a good approximation of the average conditions. MP-4L is located 50 ft downgradient of the air sparge system, which equates to a 20-day travel time if the groundwater velocity is assumed to be 2.5 ft/day. Typical concentrations of iron and arsenic at MP-4L are approximately 2.9 mg/L and 0.15 mg/L, respectively, while the air sparge system was fully operational and providing a good supply of oxygen to the groundwater. Assuming an initial DO concentration of 2 mg/L and an equilibrium pH of 5.5, the model predicted a dissolved iron concentration of 3 mg/L after 20 days, which is a reasonable approximation of the dissolved iron at MP-4L.

The iron that precipitated out of solution between the line of air sparge wells and MP-4L was assumed to be HFO. Additionally, a very small percentage of iron in the soil (less than 1%) was modeled as HFO, and the oxidation of As(III) was assumed to be insignificant. The oxidation of As(III) was removed from the PHREEQC database in the same way it was for simulations involving anoxic conditions. Under air sparge



Figure 3.14 Simulated iron concentrations: Pre-air sparge conditions.

conditions, the model predicts a dissolved arsenic concentration of 0.14 mg/L, which is very close to what is observed at MP-4L. Using these model assumptions, 80% of the arsenic that is removed from the groundwater sorbs to the freshly precipitated iron while only 20% sorbs to iron oxides in the soil.

Considering the variability in iron and arsenic concentrations observed at MP-1L, which served as initial conditions for the model, the model provides a very reasonable approximation of the impact of air sparging on the downgradient concentrations of dissolved iron and arsenic. However, it should be noted that some of the soil downgradient of the air sparge system contains elevated concentrations of arsenic (above 100 mg/kg), which could impact the concentrations of dissolved arsenic measured in the monitoring wells. Since modeling the release of arsenic from soil with elevated initial concentrations is beyond the scope of this investigation, the model results are not expected to precisely predict the observed arsenic concentration downgradient of the air sparge system in locations where soil contains high levels of arsenic.

3.4 Sources of Uncertainty

Although the model replicated iron and arsenic concentration data collected in the lab and in the field, several sources of uncertainty exist. Future modeling work could focus on quantifying the sensitivity of the model results to changes in input parameters for which there is some uncertainty. This section lists the sources of uncertainty encountered during laboratory tests and geochemical modeling.

- 1) Effort was made to mimic the in-situ site conditions as much as possible when conducting batch and column tests in the lab. Exposure of the groundwater to oxygen was minimized by filling containers from the bottom up and allowing the containers to overflow when collecting groundwater used in batch and column tests. Groundwater collection bottles were capped with no head space and only opened once placed inside an anaerobic chamber. Throughout the duration of the batch and column tests, bottles containing groundwater were only opened inside the anaerobic chamber. However, it is possible that some contact with air occurred either during initial groundwater collection or by seepage through seals on bottles while the bottles were not inside the chamber. It is known that the oxygen in groundwater collected from MW75S is generally low, but there was no way to precisely measure changes in oxygen concentration throughout the batch and column tests. To some extent, DO was used as a model calibration parameter in order to match the observed rate of iron oxidation, but this value was not adjusted beyond what could be considered reasonable.
- 2) The potential impact of photo oxidation on batch test results is unknown. Exposure of the groundwater to light was minimized by covering bottles with foil, but some light exposure was unavoidable during groundwater collection and batch and column test sampling.
- 3) Some degassing of CO₂ is unavoidable under ambient laboratory conditions. Groundwater in the vicinity of MW75S is supersaturated with CO₂ due to biological activity. Once groundwater is removed from the aquifer, changes in pressure and temperature as well as groundwater handling (mixing, pouring, pumping, etc.) lead to degassing, which can also impact the pH of the groundwater. Since there is no reasonable way to measure the extent of degassing of CO₂ during the laboratory tests, this parameter was adjusted to achieve model calibration. Degassing of CO₂ is not expected to occur under non-air-sparge ambient field conditions.

- 4) Not all processes impacting pH were included in the model simulations, and, because of this, the model is not expected to precisely match the measured pH. In some model simulations, the pH of the solution was fixed to the final measured pH. This was mostly the case in model runs simulating the batch tests involving pH adjustment with H₂SO₄ or NaOH. Although it is known that the pH of the groundwater has some impact on sorption of arsenic and the rate of iron oxidation, the sensitivity of the model calibration to the final pH value was not specifically explored.
- 5) Soil collected from the Vineland Chemical Company Site was used in the batch and column tests. Although sampling of the soil for iron and arsenic confirmed that the concentrations of these parameters did not vary significantly among the batch and column tests, the soil samples were not completely homogeneous. Calculations of model inputs such as sorption surfaces and Fe(III) contributing to the rate of iron oxidation were based on the selection of one value for iron concentration. The sensitivity of the model calibration to potential variation in the soil iron concentration has not been explored.
- 6) Measurement errors of soil mass and groundwater volume could have impacted the overall calibration results. PHREEQC performs calculations on a molar basis for a particular control volume. Both soil mass and groundwater volume are incorporated into the calculation along with concentrations of each chemical constituent to determine how many moles of iron, arsenic, etc. are involved in each model simulation. The extent to which changes in soil mass and groundwater volume impact the overall model results have not yet been explored.
- 7) The soil used in the batch and column tests was stored inside of the anaerobic chamber until it was needed. A slight change in soil color was noted after it had been inside the anaerobic chamber for some time. Some of the soil, which was originally tan to orange, developed a greyish tint, suggesting the formation of iron minerals different than those naturally found in the subsurface.



SECTION 4 Summary and Conclusion

After a P&T system for arsenic treatment could not meet the long-term remediation goals established in the Vineland Chemical Company Superfund Site ROD, a more sustainable approach was pursued which involved immobilizing arsenic in-situ with an air sparge system. The success of in-situ remediation requires a comprehensive understanding of the processes controlling the transport of arsenic. The purpose of this study was to determine the processes responsible for arsenic immobilization at the site through the collection and evaluation of site groundwater and soil data, bench-scale testing, and geochemical modeling. The evaluation successfully identified the processes controlling immobilization, as well as other key factors that contributed to the sustainable operation of the air sparge system.

Key findings include:

1) As(III) is removed from solution by sorption to HFO and iron in soil.

As(III) can sorb to iron oxides without first being oxidized to As(V). The presence of As(III) in site soil samples provides direct evidence that this process is occurring. The process of As(III) sorption to HFO was successfully modeled using the surface complexation model available in PHREEQC. Indirect evidence through modeling shows that only a small portion of arsenic partitions to iron already in the soil, and the majority of arsenic partitions to the freshly oxidized Fe(II) (HFO). Arsenic sorption to HFO is believed to be the main mechanism for arsenic attenuation in groundwater at the Vineland Chemical Company Site. Direct evidence to confirm this hypothesis could be gathered through bench-scale testing of ironpoor arsenic impacted groundwater with the site soil.

2) The rate of HFO formation is highly dependent on pH.

Fe(II) oxidation and precipitation is not rapid at pH values below 6.5. The pH of groundwater at the Vineland Chemical Company Site downgradient of the air sparge system is controlled by oxidation of iron, which decreases pH and degassing of CO_2 in the presence of air bubbles, resulting in increased pH. The native soil also has some buffering capacity. The process of iron oxidation was successfully modeled as a function of DO and pH using a non-equilibrium kinetic rate equation.

3) HFO can transform into the more thermodynamically and more crystalized minerals goethite and hematite over time.

Both goethite and hematite were found in soil samples collected from the Vineland Chemical Company Site upgradient and downgradient of the air sparge system. Goethite is encountered at a higher frequency and mass fraction as compared to hematite. This is attributed to the formation and growth mechanisms of goethite. However, it is unknown how quickly the transformation of HFO to goethite and hematite can occur under site-specific conditions, which impacts the long-term stability of the arsenic immobilized by the air sparge system. Arsenic can desorb more easily from HFO than from more crystalline iron oxides. Further investigation is needed to understand the rate of arsenic desorption if the air sparge system is turned off.

4) It is desirable to control the rate of iron oxidation to optimize in situ system performance.

Post air sparging, the pH of the groundwater at the Vineland Chemical Company Site ranged between 5.5 and 6.5, which ultimately controlled the rate of iron oxidation. At this pH range, iron precipitated out of solution downgradient of the air sparge system, eliminating potential problems due to iron fouling of the sparge wells. An elevated pH at the air sparge line would result in virtually instantaneous precipitation of iron which could lead to clogging of the system.

Maintaining a pH between 5.5 and 6.5 allows iron to precipitate downgradient of the air sparge line but before discharging to surface water. Since iron and arsenic are removed concurrently from groundwater, dissolved arsenic concentrations were also reduced before the arsenic plume reached the surface water compliance point.

The principles controlling iron oxidation and arsenic immobilization are not unique to the Vineland Chemical Company Site. Air sparging for arsenic immobilization can be applied to other sites where iron is present in groundwater in sufficient quantities, and a similar procedure of groundwater and soil characterization combined with bench-scale testing and modeling can be applied to identify the parameters most influential on pH and iron oxidation rates.

The factors that control the rate of iron oxidation can also be utilized to optimize any remedial approach where iron removal is desired, such as abandoned mine drainage (AMD) sites. Understanding these factors can allow for pH control so that iron is removed at a rate that will reduce maintenance needs due to iron fouling and also meet water quality standards at compliance points.

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