



ENGINEERING SERVICE CENTER
Port Hueneme, California 93043-4370

**TECHNICAL REPORT
TR-2306-ENV**

**COST AND PERFORMANCE REPORT FOR A PERSULFATE
TREATABILITY STUDY AT NAVAL AIR STATION NORTH
ISLAND**

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August 2008

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REPORT DOCUMENTATION PAGE

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1. REPORT DATE (DD-MM-YYYY)		2. REPORT TYPE		3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE COST AND PERFORMANCE REPORT FOR A PERSULFATE TREATABILITY STUDY AT NAVAL AIR STATION NORTH ISLAND				5a. CONTRACT NUMBER N62473-07-D-4013	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Arun Gavaskar, Battelle Wendy Condit, Battelle Karla Harre, NAVFAC Engineering Service Center				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Commanding Officer NAVFAC Engineering Service Center 1100 23 rd Avenue Port Hueneme, CA 93043				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Commanding Officer NAVFAC Engineering Service Center 1100 23 rd Avenue Port Hueneme, CA 93043				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution is unlimited					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT A pilot treatability study of persulfate was conducted at Operable Unit 20, Naval Air Station North Island between November 2006 and June 2007. The treatment was targeted for removal of chlorinated volatile organic compounds (CVOCs) from groundwater (primarily trichloroethylene) located at a depth of up to 54 ft below ground surface. This report summarizes the cost and performance data from this treatability study.					
15. SUBJECT TERMS Dense, non-aqueous phase liquid (DNAPL)					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER (include area code)

**Cost and Performance Report for a
Persulfate Treatability Study
at Naval Air Station North Island**

**Contract Number: N62473-07-D-4013
Task Order: 007**

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EXECUTIVE SUMMARY

The objective of this cost and performance report is to summarize the results, review the performance, and draw lessons learned for future applications from the persulfate injection pilot test conducted at Operable Unit 20 (OU-20), Naval Air Station (NAS) North Island in San Diego, California.

The pilot injection test of persulfate was conducted at the Building C-40 site located within OU-20 NAS North Island between November 2006 and June 2007. The treatment was targeted in a chlorinated volatile organic compound (CVOC) source area with groundwater containing primarily trichloroethylene (TCE). The field pilot tests were conducted after site-specific bench-scale tests showed that persulfate would be effective at this site. The generation of the highly reactive sulfate radical was reported to have been initiated by low temperature heat activation at ambient groundwater temperature (20 to 24 °C). The persulfate and sulfate radicals are strong oxidants that react with reduced organic matter (and CVOC contaminants) to form sulfate ions.

Site lithology consists of interbedded layers of poorly graded fine to very fine sand and silty sand. The depth to groundwater ranged from 19.3 to 20.3 ft below ground surface (bgs) and groundwater was present as an unconfined aquifer at this site. The pilot treatment was targeted at a 10-foot depth interval of 44 to 54 ft bgs, where much of the CVOC contamination was sequestered.

Persulfate was introduced into the target aquifer zone through a recirculation system consisting of four extraction wells located at the corners of a diamond-shaped treatment area, along with an injection well in the center. The oxidant was injected continuously for the most part from January 26 to February 1, 2007. Four performance monitoring wells were also installed between the central injection well and each of the extraction wells. An additional monitoring well was installed just beyond the downgradient edge of the array to monitor for potential downgradient migration of contaminants or oxidant. Soil vapor probes were also installed at the site to monitor any CVOCs escaping into the atmosphere.

There was an immediate sharp decline in the TCE levels at the site following the day 7 and 19 post-treatment monitoring. However, the monitoring wells within the treatment zone exhibited varying levels of rebound. This sharp decline in TCE levels immediately following oxidant injection indicated that the oxidant distribution was successful. The subsequent rebound appears to be largely due to influx of contaminated groundwater from the surrounding aquifer. The wells further away from the central injection point showed relatively slower decline in the contaminant levels than the wells in the immediate vicinity of the injection point. Oxidation reduction potential (ORP), dissolved oxygen (DO), and pH responded sharply to the persulfate injection. ORP rose sharply in several wells, whereas pH declined sharply. These trends are along expected lines for generation of strongly oxidizing conditions in the aquifer. The oxidizing conditions also remobilized certain trace metals in the aquifer.

There are certain limitations to the technology such as the continued co-existence of both TCE and residual persulfate in many of the treatment area wells (and in many cases, rebound of TCE levels) towards the end of the 60-day and 90-day post-treatment monitoring periods. This phenomenon may indicate that in addition to a stoichiometric presence of persulfate in the groundwater, some threshold concentration of persulfate may be required to initiate CVOC-persulfate reactions or at least drive the kinetics of the reactions to a level where further declines in TCE are noticeable. Furthermore, the lower levels of persulfate reaching the wells further away from the injection point may indicate retardation of the oxidant by CVOCs and natural organic matter in the soil. The decline of TCE and cis-DCE concentrations in these wells was substantial, but not as much as in the closest wells. This is to be expected and follows the typical cost-benefit tradeoff between the costs of longer time in the field and greater chemical usage versus the benefit of additional CVOC removal.

The total cost of the project was \$170,173. For the 889 cubic yards of aquifer targeted, the unit cost of treatment is approximately \$191/cubic yard, which is cost competitive with most other in-situ treatment technologies that involve injection of a reagent into the subsurface. With a maximum treatment depth of 54 ft bgs in moderately permeable soils, this site may be said to present a moderate challenge for reagent distribution remediation, compared to other sites. Site preparation and mobilization were the largest components of the total cost.

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ACRONYMS AND ABBREVIATIONS

bgs	below ground surface
CVOC	chlorinated volatile organic compound
DNAPL	dense, non-aqueous phase liquid
DO	dissolved oxygen
ORP	oxidation reduction potential
OU	operable unit
TCE	trichloroethylene

Section 1.0: INTRODUCTION

The objective of this cost and performance report is to summarize the results, review the performance, and draw lessons learned for future applications from the persulfate injection pilot test conducted at the Building C-40 site, Operable Unit 20 (OU-20), Naval Air Station North Island, San Diego, California. The pilot test field activities were conducted between November 2006 and June 2007 (Shaw, 2007). The treatment was targeted in a source area with groundwater containing chlorinated volatile organic compounds (CVOCs), primarily trichloroethylene (TCE). The field pilot tests were conducted after site-specific bench-scale tests showed that persulfate would be effective at this site. The generation of the highly reactive sulfate radical was reported to have been initiated by low temperature heat activation at ambient groundwater temperature (20 to 24 °C) in this site. Persulfate and sulfate radical are strong oxidants that react with reduced organic matter (and CVOC contaminants) to form sulfate ion.

Section 2.0: GEOLOGY AND HYDROGEOLOGY

Site lithology identified during the installation of the monitoring wells indicates that the unconfined surficial aquifer at this site consists of interbedded layers of poorly graded fine to very fine sand and silty sand. Shell fragments were identified in the majority of the well borings. These soils are part of the Bay Point Formation. The depth to groundwater in March 2007 ranged from 19.3 to 20.3 ft below ground surface (bgs). The pilot treatment was targeted at a 10-foot depth interval of 44 to 54 ft bgs, where much of the contamination is sequestered. The aquifer continues several feet deeper below the target treatment zone. It is unclear why the highest contamination is associated with depths that are several feet above the aquitard.

Regional groundwater flow is towards the northeast with a relatively flat hydraulic gradient of 0.001 ft/ft. Accessibility (absence of aboveground buildings, minimum disruption of traffic, etc.) was a major factor in selection of the pilot site at the intersection of Quentin Roosevelt Boulevard and 1st Street (see Figure 1).

Section 3.0: CONTAMINANT DISTRIBUTION

The primary CVOCs detected in direct-push groundwater samples and their maximum concentrations are:

- TCE (6,800 µg/L)
- Cis-1,2 DCE (2,300 µg/L)
- 1,1 DCE (160 µg/L).

The highest TCE concentration in the direct-push groundwater sampling occurred in OU20-DB-06 (see Figure 1). The highest detected TCE soil concentration (220 µg/kg) was observed at OU20-PEW-6 at 49.5 ft bgs. The highest groundwater baseline (pre-treatment) TCE concentration in the monitoring wells occurred in OU20-PMW-9 (16,500 µg/L). In Figure 1, a north-south oriented oval area encompassing these points of high TCE concentration was the targeted treatment area. The highest TCE concentration of 16,500 µg/L is higher than the threshold concentration (1% of solubility) generally accepted as indicative of DNAPL. Elevated concentrations of TCE are present both upgradient and downgradient of the target treatment area, thus indicating the potential presence of additional DNAPL sources in the surrounding aquifer.

Section 4.0: TECHNOLOGY IMPLEMENTATION

Persulfate was introduced into the target aquifer zone through a recirculation system consisting of four extraction wells (O20-PEW-5, OU20-PEW-6, OU20-PEW-7, and OU20-PEW-8) at the approximate corners of a diamond shaped area and an extraction well (OU20-PIW-2) in the center. The northern and southern extraction wells are further apart than the eastern and western extraction wells. These wells have 10-foot screens targeted at the 44 to 54 ft bgs interval for treatment. The target treatment volume was estimated at a size of 36 ft wide (between eastern and western extraction wells), 60 ft long (between northern and southern extraction wells) and 10 ft thick. At an estimated porosity of 28%, this equates to a pore volume of 36,194 gal.

The primary components of the injection system consisted of transfer pumps, a system manifold to receive the extracted groundwater, a pre-filtration element to remove sediment from the water, a mixer to mix the persulfate with the extracted water, and a post-filtration element to remove particulates from the injected fluids. Based on bench-scale results, a 3 to 6% solution of persulfate was determined to be desirable and a 4.5% was targeted for the field application. A total of 22,646 lbs of sodium persulfate was mixed with 60,000 gal of groundwater extracted from the edges of the treatment zone and injected back in the aquifer.

The oxidant was injected continuously for the most part from January 26 to February 1, 2007. The initial groundwater extraction rates were 3 gpm (from the northern and southern extraction wells) and 2 gpm (from the eastern and western extraction wells) for a total injection rate of 10 gpm. Each batch of treated groundwater consisted of approximately 1,020 gal of groundwater mixed with 386 lbs of oxidant. Potassium iodide starch paper was used to gauge how far persulfate had traveled in the aquifer from the central injection well.

Section 5.0: PERFORMANCE EVALUATION APPROACH

Four performance monitoring wells (OU20-PMW-06 to -09) were installed between the central injection well and each of the extraction wells. A soil vapor probe was installed at OU20-PVP-1. An additional monitoring well (OU20-PMW-10) was installed just beyond the downgradient edge of the array to determine any downgradient migration of contaminants or oxidant. All monitoring wells have 10-foot screens at the target treatment interval. Aquifer slug tests were conducted before and after treatment in injection and extraction wells. Water level measurements were conducted on March 19, 2007.

Following a baseline (pre-treatment groundwater sampling event) on January 9-11, 2007, post-treatment monitoring was conducted 7, 19, 30, 60, and 90 days following the final injection of persulfate (February 8, February 20, March 5, April 4, and May 2).

In addition to the CVOCs, groundwater samples were analyzed for field parameters (DO, ORP, pH, conductivity) and a whole host of geochemical parameters (including trace metals).

Section 6.0: TECHNOLOGY PERFORMANCE

Figure 2 shows the TCE and cis-1,2 DCE trends in the performance monitoring wells. TCE levels showed a sharp decline especially in the 7-day and 19-day post-treatment events, following which the wells showed varying degrees of rebound. This sharp decline in TCE levels immediately following oxidant injection, along with other indicators, showed that the oxidant distribution was successful. The subsequent rebound appears to be largely due to influx of contaminated groundwater from the surrounding aquifer. PMW-6 and PMW-8 showed the sharpest decline in both TCE and cis-1,2 DCE. These are the two wells closest to (approximately 10 ft from) the central injection point. PMW-7 and PMW-9, which are relatively further away (approximately 20 ft) from the injection point did not show as sharp a decline, although TCE concentrations continued to decline well into the 60 and 90 day post-treatment periods in these wells. This indicates that oxidant persisted in the aquifer for a considerable time. As expected, TCE and cis-1,2 DCE levels declined sharply in the injection well PIW-2, often to non-detect levels.

Figure 3 shows the residual persulfate concentrations in the wells at different times. The persulfate data are congruent with the TCE data. The wells with the highest persulfate residuals (PIW-2, PMW-6, and PMW-8) are also the ones showing the greatest TCE declines and are closest to the injection well. More distant wells, such as PMW-7 and PMW-9, as well as eventually PMW-10, indicate the arrival of the residual persulfate front. At the end of the 90-day period, there still was residual persulfate in all treatment area wells. The fact that residual persulfate co-exists with stable or increasing TCE levels in several wells, such as PEW-5, may indicate that a certain threshold level of persulfate may be required to initiate oxidation reactions responsible for TCE destruction. PEW-5 was the only well that did not show any substantial TCE decline following the treatment, indicating that persulfate distribution in this region may have been limited. On the other hand, TCE levels declined initially in PMW-8, but rebounded sharply during later monitoring events, despite high levels of residual persulfate reaching this well.

Oxidation reduction potential (ORP), dissolved oxygen (DO), and pH (see Figures 4 and 5) responded sharply to the persulfate injection. ORP rose sharply in several wells, whereas pH declined sharply. These trends are along expected lines for generation of strongly oxidizing conditions in the aquifer. However, it is difficult to correlate TCE treatment performance with residual persulfate, ORP, or pH levels in individual wells.

Chloride and sulfate (see Figure 6) rose sharply in several wells. The sharp increase in sulfate levels is accounted for by the fact that persulfate reacts with reduced organic matter (and CVOCs) to form sulfate. The sharp increase in chloride levels in some wells, such as PMW-10, PEW-8, and PIW-2 is harder to explain. Pre-treatment CVOC concentrations are in the few tens of mg/L, whereas pre-treatment chloride concentrations ranged from 220 to 1,520 mg/L. It would be difficult for any chloride generated from CVOC degradation to have a noticeable impact on native chloride levels.

Figures 7, 8, and 9 show metals concentrations in the groundwater. Dissolved iron rose sharply in some wells and manganese levels decline sharply in all wells. The sharp drop in manganese is another indication of the strongly oxidizing conditions that convert Mn (II) to Mn (IV), which precipitates out as manganese dioxide. Typically native dissolved iron may be expected to precipitate out (decline) under strongly oxidizing conditions, but in this case the source of iron may be mineral in origin. Dissolution of reduced mineral species, such as pyrite and other ores, under strongly oxidizing conditions may be contributing to increases in both dissolved iron and sulfate, as well as to increase in arsenic, vanadium, and chromium. Although the geochemical environment (pH, ORP, and DO levels) has rebounded to pre-treatment conditions, many of these metals continue to remain substantially elevated. The fate of these metals needs to be tracked during additional monitoring events in the treatment zone wells, and perhaps in wells that are further downgradient too.

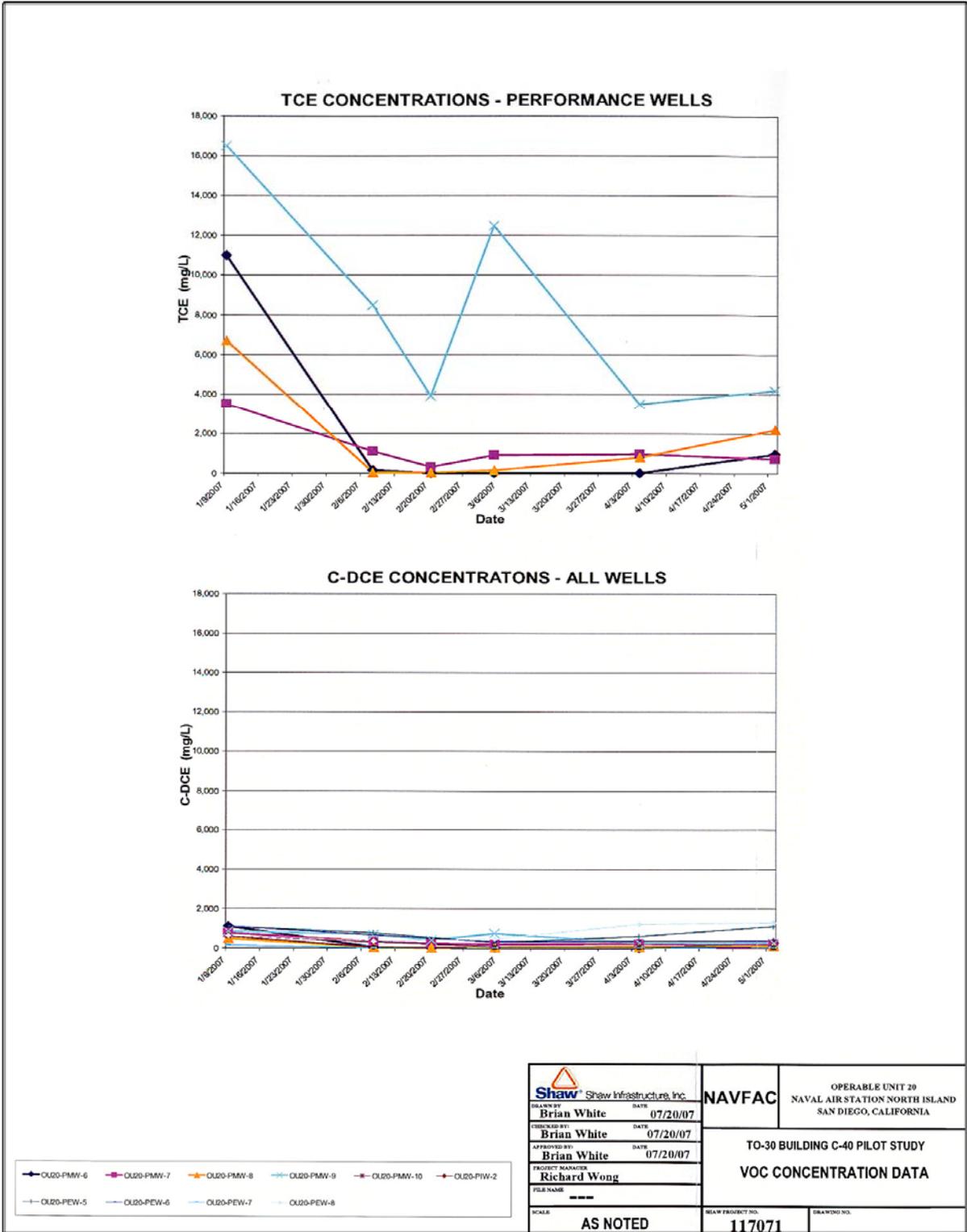


Figure 2. TCE and cis-1,2 DCE in Treatment Area Wells

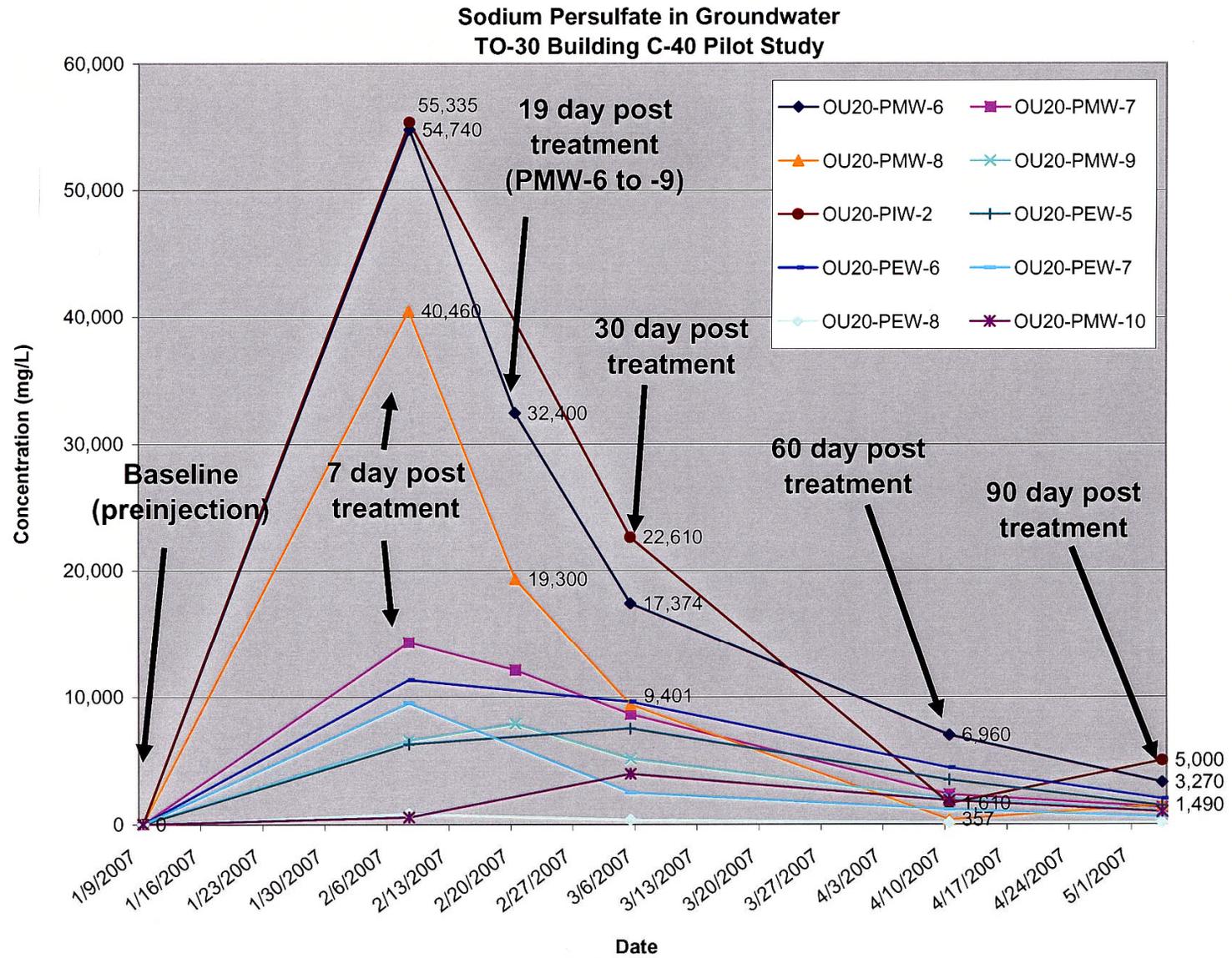


Figure 3. Residual Persulfate Levels in Treatment Area Wells

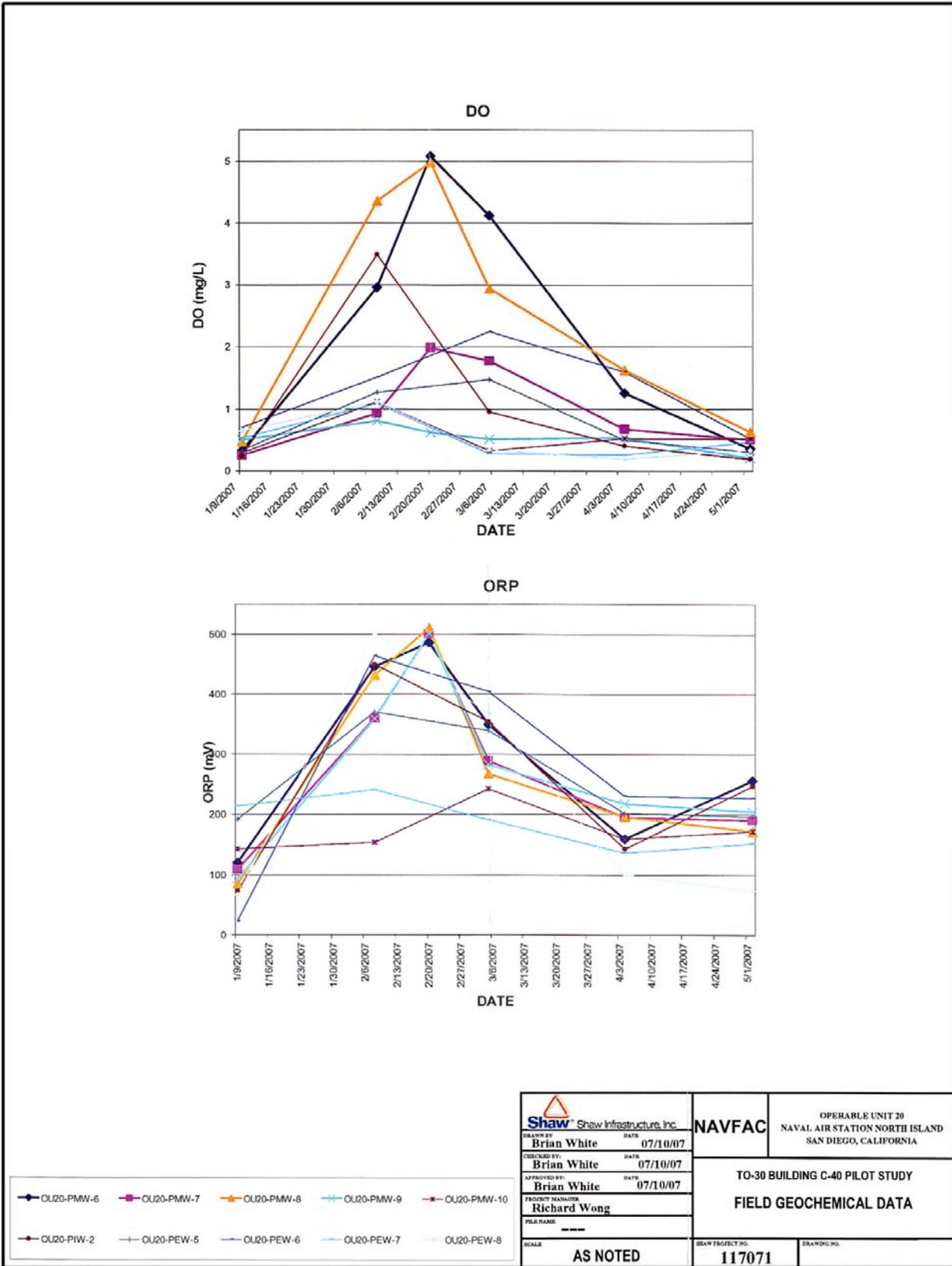
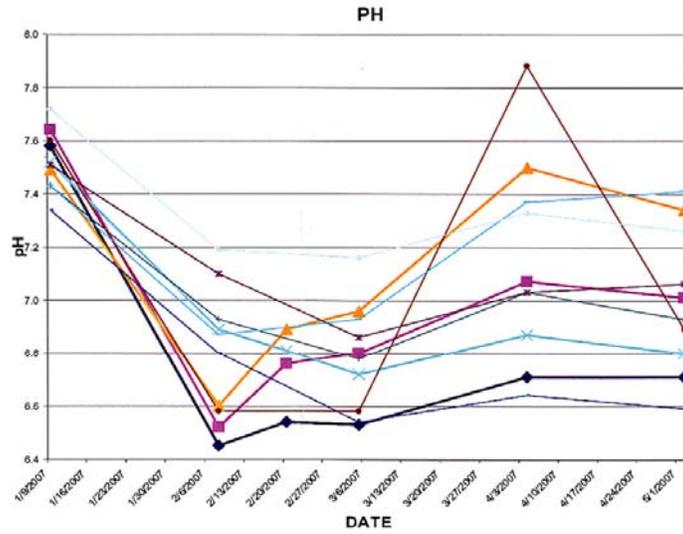


Figure 4. DO and ORP



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Figure 5. Groundwater pH

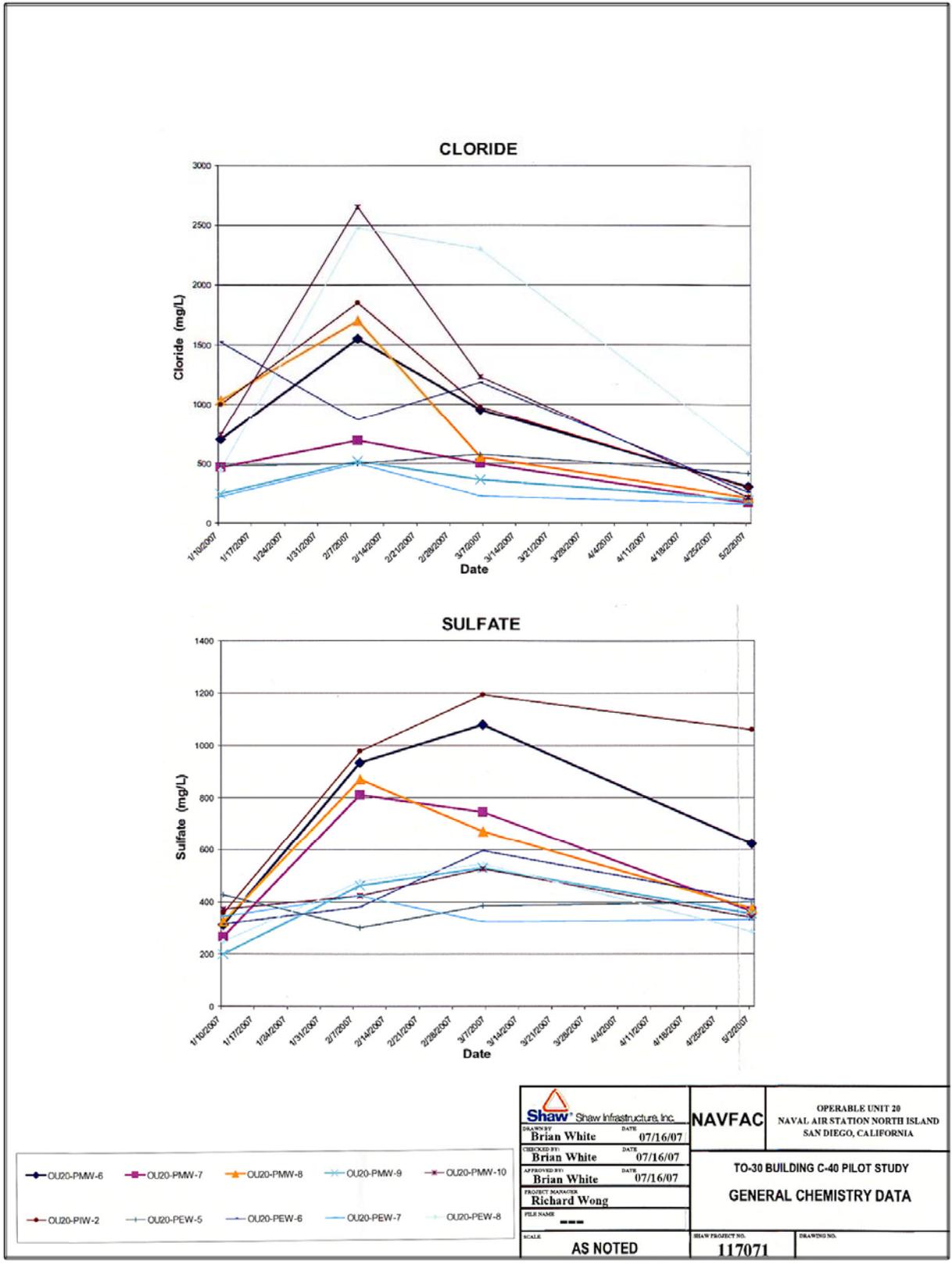
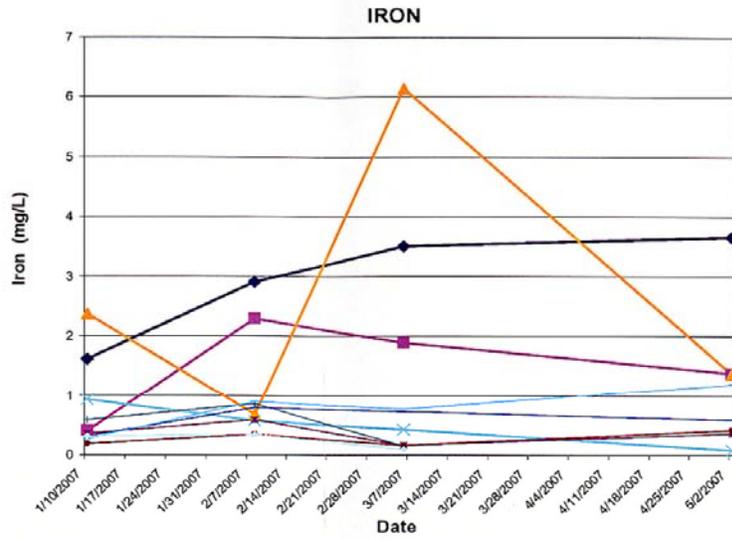
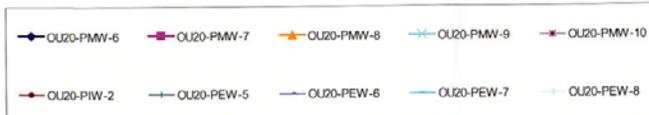
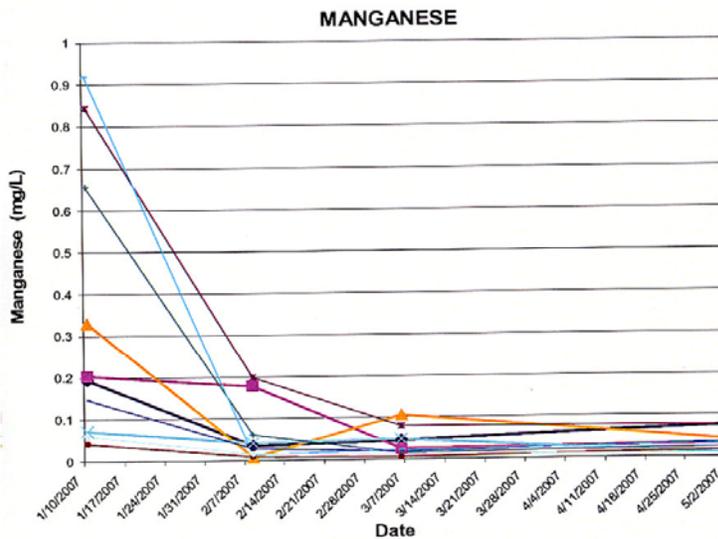
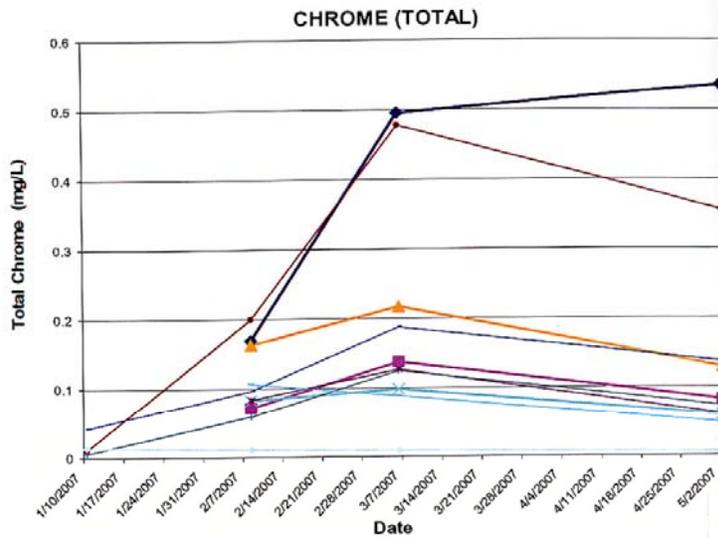


Figure 6. Chloride and Sulfate



		NAVFAC	OPERABLE UNIT 20 NAVAL AIR STATION NORTH ISLAND SAN DIEGO, CALIFORNIA
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Figure 7. Dissolved Iron



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	DATE: 07/16/07	TO-30 BUILDING C-40 PILOT STUDY METALS DATA 3 OF 3
	SCALE: AS NOTED	DRAWING NO.: 117071

Figure 8. Chromium and Manganese

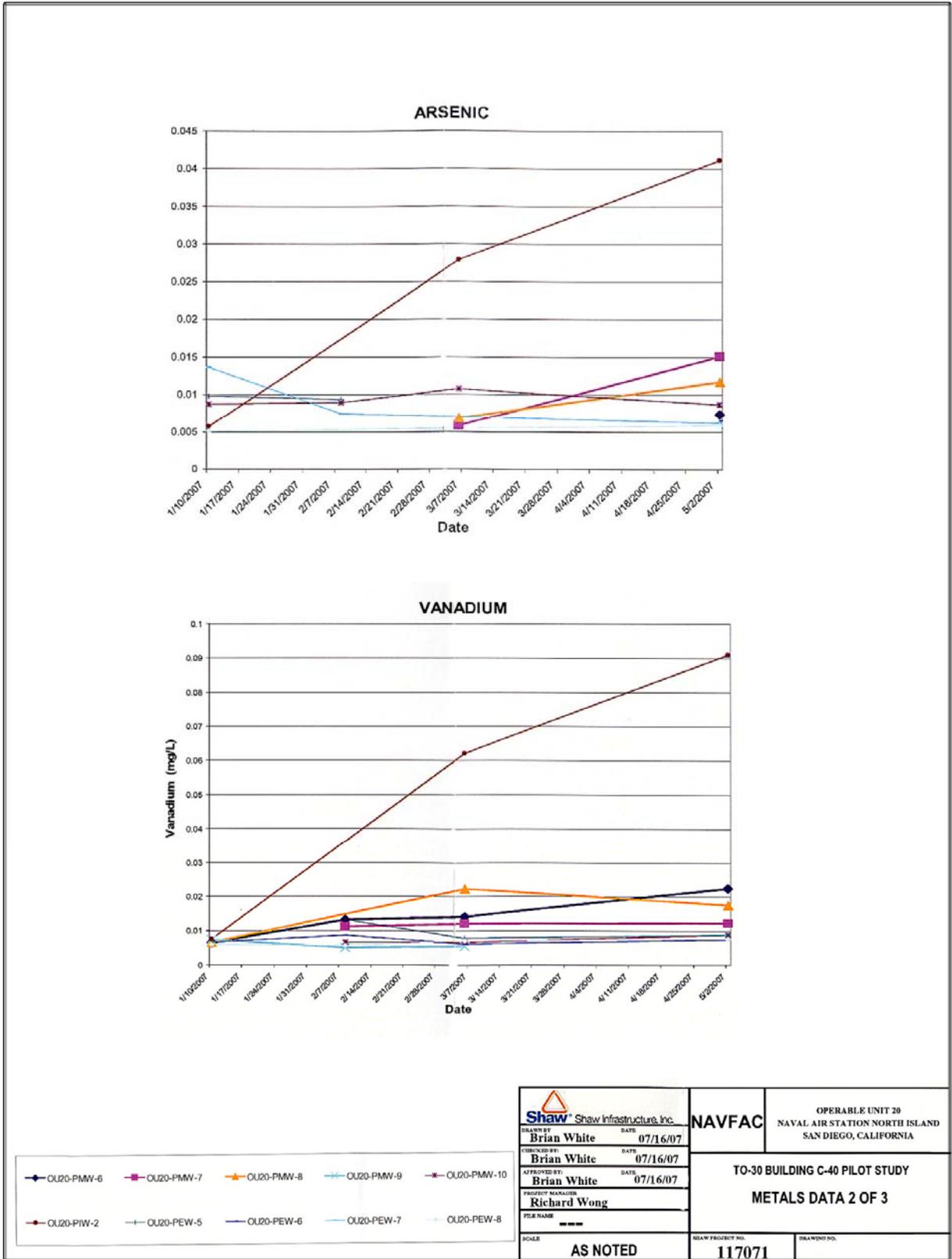


Figure 9. Arsenic and Vanadium

As seen in Table 1, slug tests conducted in the treatment zone wells before and after persulfate treatment showed that the hydraulic conductivity did not change much, except in PEW-07, the reason for which is unclear. The slug tests were conducted in the injection and extraction wells only. Water entering the injection well had been filtered twice, once before and once after the persulfate mixing tank. So any suspended solids would have been removed during the recirculation. The bench-scale tests had indicated the possibility that calcium sulfate solids generated when persulfate reacts with native alkalinity (calcium carbonate) in the groundwater could be significant. However, in this recirculation-filtration mode, this does not appear to have been a problem. It would have been interesting to analyze the solids deposited on the filters for calcium. It would have been interesting to see slug test results for some of the performance monitoring wells, especially PMW-6 and PMW-8, which are close to the injection well and which probably received the strongest dose of persulfate.

Table 1. Slug Test Results

Well	Date*	Average Hydraulic Conductivity (ft/day)
PIW-02	Jan-07	0.58
	Mar-07	0.69
PEW-05	Jan-07	22.44
	Mar-07	25.24
PEW-06	Jan-07	22.85
	Mar-07	26.11
PEW-07	Jan-07	73.99
	Mar-07	14.83
PEW-08	Jan-07	31.47
	Mar-07	30.20

* Pre-treatment (January) and post-treatment (March)

Section 7.0: COST

The objective of the cost summary in Table 2 is to enable a comparison costs for different technologies on an equivalent basis. Therefore, costs that are site-specific or situation-specific, such as work plan preparation, design, planning, permitting, and monitoring, have been excluded. The focus is on the cost that is required to mobilize to the site, conduct the treatment, and demobilize. A total treatment cost for the project is estimated by adding the capital investment and operating cost. Next, a unit cost of treatment is estimated based on the volume of aquifer targeted for treatment. This is based on two assumptions driven by past experience with such projects. One is that most, if not all, treatments seek to create conditions conducive to the removal of contamination in a given volume of aquifer and that this volume is a bigger driver of the treatment cost than the contaminant mass (which can be subject to poor initial estimates, different degrees of post-treatment residuals, etc.). Second, the assumption is that the volume targeted for treatment is more relevant than the volume actually claimed to be treated. Often, the reagent injected may migrate beyond the boundaries of the target treatment zone, but this extra volume is not included. Finally, the maximum depth of treatment and geology of the site are qualitative/semi-quantitative measures that drive degree of difficulty and treatment costs need to be calibrated against these measures.

Table 2 shows that the total cost of the project was \$170,173. For the 889 cubic yards of aquifer targeted, the unit cost of treatment is approximately \$191/cubic yard, which is cost competitive with most other in-situ treatment technologies that involve injection of a reagent into the subsurface. With a maximum treatment depth of 54 ft bgs in moderately permeable soils, this site may be said to present a moderate challenge for reagent distribution remediation, compared to other sites. Site preparation and mobilization were the largest components of the total cost.

Table 2. Cost of Persulfate Application at NAS North Island

No.	Item	Unit	No. of Units	Unit Cost	Cost
CAPITAL INVESTMENT (Fixed Cost)					
1	Site preparation (utility lines, concrete pad, etc.)	Dollar	1.00	\$88,481	\$88,481
2	Mobilization/demobilization (transportation to site, storage, fabrication, assembly, setup, dismantle)	Dollar	1.00	\$18,646	\$18,646
3	Equipment purchase (total cost if one time use; amortized cost if plan to use at multiple sites)	Dollar	1.00	\$14,454	\$14,454
4	Labor (for transportation, on-site setup, unless included in mobilization)	Hr	150.00	\$38	\$5,682
5	Other				\$0
TOTAL CAPITAL					\$127,263
OPERATING COST (Variable Cost)					
6	Equipment leasing (e.g., storage tanks, pumps)	Dollar	1	\$5,492	\$5,492
7	Chemicals/reagents	Pound	1.16	\$15,125	\$17,485
8	Other consumables (estimated)			\$500	\$500
9	Power (base provided)				\$0
10	Other utilities (base provided)				\$0
11	Waste disposal (taken to base IWP)	Gallon	275	\$0.10	\$28
12	Labor (for operating the system)	Dollar	1	\$19,406	\$19,406
13	Other				\$0
TOTAL OPERATING COST					\$42,910
TOTAL TREATMENT COST FOR PROJECT					\$170,173
	Volume of Aquifer Targeted for Treatment			Cu yd	889
	Unit Cost of Treatment			\$/Cu yd	\$191
	Max. Depth of Treatment			ft bgs	54
<p>Site Geology : Site lithology in the pilot test area consists primarily of interbedded layers of poorly graded fine to very fine grained sand and silty sand. The depth to groundwater is approximately 20 feet bgs. The aquifer is unconfined.</p>					

Section 8.0: DISCUSSION

The field pilot test was well designed and well implemented, with performance monitoring that was comprehensive in evaluating various important aspects of the persulfate application. There is a fair amount of evidence from the pilot test that the persulfate application succeeded in substantially treating the primary CVOCs, TCE and cis-DCE, present in the target aquifer zone at this site:

- The sharp decline in TCE and cis-DCE levels in all probability can be attributed to reaction with the persulfate.
- Residual persulfate levels were highest in the injection well (PIW-2) and in the two wells closest to the injection well (namely, PMW-6 and PMW-8). The degree of decline in groundwater TCE levels exactly matches this persulfate distribution, with the greatest declines occurring in PIW-2, followed by PMW-6 and PMW-8.
- Residual persulfate did not reach as high a level in wells PMW-7, PMW-9, PEW-5, and PEW-7, which are further away (along the longer axis of the elongated oval treatment area). Presumably, the more concentrated core of the persulfate front had not reached these locations in the 90-day period, perhaps retarded by CVOCs and natural organic matter in the soil. The TCE and cis-DCE declines in these wells are substantial, but not as much as in the closest wells. This is to be expected and follows the typical cost-benefit tradeoff between the costs of longer time in the field and greater chemical usage versus the benefit of additional CVOC removal. A distant well, PMW-10, too showed a substantial decline in CVOC concentrations, thus indicating that the oxidant was distributing laterally and downgradient as well.
- Geochemical indicators are congruent with the achievement of good oxidant distribution. Substantially elevated ORP, DO, sulfate, and dissolved iron levels and substantially depressed pH and dissolved manganese levels all point to the creation of a strongly oxidizing environment.

The continued co-existence of both TCE and residual persulfate in many of the treatment area wells (and in many cases, rebound of TCE levels) towards the end of the 60-day and 90-day post-treatment monitoring periods may indicate that in addition to a stoichiometric presence of persulfate in the groundwater, some threshold concentration of persulfate may be required to initiate CVOC-persulfate reactions or at least drive the kinetics of the reactions to a level where further declines in TCE are noticeable. In other words, below a certain threshold persulfate concentration, the ability of any remaining persulfate in the aquifer to drive additional CVOC treatment may be minimal.

Chloride is theoretically the best indicator of CVOC treatment because generation of chloride attributable to CVOC destruction can help eliminate the possibility that the observed decline in CVOC may be due to dilution from influx of cleaner water from the surrounding aquifer. However, in many field situations where native chloride levels are relatively high to begin with, the impact on chloride levels attributable to CVOC destruction is difficult to gauge. This may be the case at this site too. Chloride levels increased in some wells, declined in others, and remained approximately the same in some wells. This may simply indicate a redistribution of chloride due to the pumping and recirculation of the groundwater among the wells. Extraction wells PEW-6 (4,100 ug/L) and PEW-7 (2,600 ug/L) had much lower baseline (pre-treatment) TCE levels compared with PEW-5 (11,000 ug/L) and PEW-8 (10,000 ug/L), under static conditions. There are no data on TCE levels in these wells or in the manifold that combines the extracted water from these wells and leads it to the persulfate mixing tank, during the persulfate injection. In the post-treatment sampling, TCE levels in PEW-5 and PEW-6 did not change

considerably. In PEW-8, there is some post-treatment decline in TCE levels and in PEW-7, there is a sharper decline in TCE. Again, it is difficult to attribute the decline in TCE in these extraction wells along the edge of the treatment zone to either dilution or treatment. If data were available on the TCE levels at the inlet to the persulfate mixing tank and at the inlet of the injection well PIW-2 during the injection, they would have helped better address the TCE dilution versus treatment issue.

The trace metals levels in the treatment zone groundwater may be worth tracking for a few more quarters. The fate of these metals is unclear. At the end of 90 days post treatment, other geochemical parameters, such as DO, pH, ORP have returned close to their pre-treatment equilibrium levels. However, trace metals, such as chromium, arsenic, and vanadium continue to remain at substantially elevated levels. The level of these metals needs to be tracked on a quarterly basis in the treatment area wells and in downgradient wells (e.g., PMW-10).

Section 9.0: REFERENCES

Shaw. 2007. *Persulfate Pilot Test Summary Report: Naval Air Station North Island Operable Unit 20, San Diego, California*. Prepared by Shaw Infrastructure, Inc. Submitted to Naval Facilities Engineering Command Southwest, San Diego, CA. November 2007.