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DEMONSTRATION OF RESIN ADSORPTION TECHNOLOGY FOR TREATMENT OF VOCs IN GROUNDWATER

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ABSTRACT

Aberdeen Proving Ground (APG) has been a center for the development, testing, and manufacture of military-related chemicals since World War I, with industrial activities concentrated in the Canal Creek Area. Groundwater at APG has been impacted by these historical practices. The APG Installation Restoration Program (IRP) is implementing the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) process throughout APG. A Record of Decision (ROD) has been completed for the East Canal Creek Area Plume, specifying groundwater extraction, treatment, and beneficial reuse or discharge of treated water.

Volatile organic compounds (VOCs) are the primary contaminants of concern in the East Canal Creek Area plume. In addition to common commercial solvents such as trichloroethylene (TCE) and its breakdown products, the East Canal Creek Area plume is contaminated with 1,1,2,2-tetrachloroethane (1,1,2,2-TeCA). Based upon preliminary treatability testing during the CERCLA Feasibility Study (FS), the treatment approach specified in the ROD includes precipitation and filtration to remove iron and manganese followed by synthetic resin adsorption with on-site steam regeneration to remove VOCs. The plant was intended to provide a supplemental potable water supply to the base or to discharge to surface water.

A predesign pilot study was conducted to evaluate resin adsorption performance, and support the design of the groundwater treatment plant for the East Canal Creek Area groundwater plume. The primary pilot test objectives were to confirm the effectiveness of the medium to remove VOCs to levels suitable for potable water beneficial reuse (Safe Drinking Water Act [SDWA] Maximum Contaminant Levels [MCLs], Maximum Contaminant Level Goals [MCLGs], or risk-based standards) or surface water discharge (National Pollutant Discharge Elimination System [NPDES]-equivalent limit, including Ambient Water Quality Criteria), and to define the capacity of the media after multiple exhaustion and regeneration cycles. The pilot plant was constructed at APG, and testing was conducted on groundwater from an existing well within the Canal Creek Area plume. Eight column exhaustion and nine regeneration cycles were completed during the testing program. The pilot treatment system included pretreatment equipment to remove iron and manganese from the groundwater followed by two columns, in series, of Ambersorb® 563 media operating in lead-lag mode to increase the treatment run length while producing final effluent containing low to non-detectable VOCs. At or near breakthrough for each test run, the lead column was regenerated with steam to remove the VOCs as a vapor, which was condensed to produce an aqueous and an organic phase. Samples were collected for VOC analysis at the first-stage influent and effluent (before and after the lead column) and the final (lag column) effluent. The principal VOCs found in the supply well for the pilot test were cis- and trans-1,2-dichloroethene (1,2-DCE), TCE, vinyl chloride (VC), and 1,1,2,2-TeCA. The total VOC concentration of the influent ranged between approximately 2,000 μg/L and 3,100 μg/L. VC is a critical parameter in the design and operation of this treatment technology because it is the first to break through the lead column, thereby defining the adsorption capacity. It is also noncondensable during regeneration and requires capture in a vapor control system.

Results of the pilot study demonstrate that with proper control of the service cycle and regeneration of the media, the selected treatment train will produce water containing no detectable VOCs for extended periods. The volumetric VOC loading capacity on the resin demonstrated by the pilot test would allow a 22-day service cycle at design contact times after each regeneration. The mass loading capacity for the limiting parameter, VC, in terms of mass VC/ft^3 of resin, was proportional to the influent VC concentration, over the range of conditions observed in the pilot test, resulting in a fixed volumetric capacity over the range of expected VC levels. Because trace metals and solids may foul the resin bed, the full-scale design was revised to incorporate a barrier filter to remove micron-size solids from the influent water to the columns. Design, construction, and startup of the facility have been completed and the facility has been in full-scale operation since April 2003. In the first 11 months of full-scale operation, approximately 71 million gallons of contaminated groundwater were treated with an average total VOC removal efficiency of 96%.

KEYWORDS

1,1,2,2-Tetrachloroethane, Ambersorb® 563, CERCLA, groundwater treatment, pilot testing, resin adsorption, resin attrition, volatile organic compound.

INTRODUCTION

A CERCLA Record of Decision (ROD) for Interim Remedial Action for the East Canal Creek Area plume specified extraction and treatment of groundwater contaminated with volatile organic compounds (VOCs), using precipitation/filtration to remove metals and synthetic adsorption media (such as Ambersorb® 563) to remove VOCs. Previous work had indicated the potential for this media to remove VOCs to low levels (Parker and Bortko, 1991; Isacof et al., 1992; Parker, 1992). Preliminary testing during the Canal Creek Feasibility Study (FS) screened the use of resin adsorption for this site (PNL, 1998). In addition, the FS-level study did not simulate the actual plant configuration intended for full-scale design. However, relatively little design and operating information was available. Only one complete cycle of resin exhaustion and regeneration was completed in previous bench-scale testing for the FS. Since virgin resin typically has higher adsorptive capacity than after subsequent regenerations, that preliminary study did not provide confirmation of long-term performance. Therefore, a pilot study was conducted, following preliminary design based upon previous literature, to confirm the effectiveness of this medium to remove VOCs to required effluent levels, and evaluate performance after multiple exhaustion and regeneration cycles. An additional objective of the study was to define the partitioning of the VOCs among the three phases produced during regeneration. Steam used for regeneration of the resin volatilizes adsorbed VOCs from the bed to be condensed, producing an organic phase and an aqueous phase. Certain VOCs are noncondensable, such as vinyl chloride (VC), and remain largely in the vapor phase. Knowledge of the distribution of VOCs in each phase would be useful in the design and operation of the full-scale treatment plant.

The treatment medium for this pilot test was Ambersorb® 563, one of a family of synthetic carbonaceous adsorbents developed by the Rohm and Haas Company (other resin products were subsequently screened for application during detailed design of the plant). The medium is composed of hard, spherical beads with high physical integrity and a high VOC-sorptive capacity, manufactured from a highly sulfonated styrene/divinylbenzene macroreticular ion exchange resin. The surface is pyrolized using a proprietary process, resulting in retention of the macroreticular structure with increased microporosity and mesoporosity. According to vendor information, this process produces a highly reproducible structure with high kinetic rates of adsorption, high adsorption capacity, and low expected attrition rates. An additional significant property of this material is that it can be regenerated in situ (i.e., within the adsorption column) using, most typically, steam, with the vapors being collected and condensed (Rohm and Haas, 1992). The condensate may be separable into an aqueous phase containing VOCs at their solubility limits, and an organic phase, a mixture of the individual VOCs. For an application such as this groundwater treatment plant, the organic phase would be disposed of off-site. Following regeneration and phase separation, superloading can be used to remove VOCs from the aqueous phase of the condensate, by passing it through the adsorption column just prior to the next regeneration. This takes advantage of the higher sorptive capacity of the resin at higher concentrations. The column effluent during this phase is only slightly above normal. Previous testing has shown that the medium can remove VOCs from groundwater at short contact times (Parker, 1992). The process was the subject of an Emerging Technology Demonstration for groundwater cleanup under the Superfund Innovative Technology Evaluation (SITE) Program (Weston, 1995), as well as pilot testing for the U.S. Air Force (Weston, 1999a).

The pilot study was conducted on-site using water from an existing groundwater plume monitor well. The pilot treatment system included pretreatment to remove iron and manganese from the groundwater followed by two Ambersorb® 563 columns in series, operating in lead-lag mode during the pilot test. Following lead column breakthrough for each test run, the lead column was regenerated with steam to remove VOCs as a vapor to be condensed for production of an aqueous/organic phase for disposal. Eight adsorption column exhaustion runs were completed, with each Ambersorb® 563 column in the lead position for four runs. The overall flow scheme corresponded to that intended for the full-scale design.

The principal VOCs included 1,1,2,2-TeCA, TCE, cis- and trans-1,2-DCE, and VC, with total VOC concentrations ranging between 2,000 μg/L and 3,100 μg/L. VC is a critical parameter in the design and operation of this treatment technology because it is the first to break through the lead column, thereby defining the adsorption capacity.

MATERIALS AND METHODS

Figure 1 shows a flow diagram for the adsorption and regeneration processes, while historical groundwater data from the previous bench-scale study from the same well are summarized in Table 1. Batches of groundwater were pretreated to remove iron and manganese and control adsorption column fouling. Pretreated groundwater was fed continuously to the adsorption train in an upflow direction. To pretreat a batch of groundwater, lime slurry was used to raise the pH to approximately 9.0. Water was then transferred to a settle/decant tank until the next batch was treated. Precipitated iron and manganese settled in the tank, leaving iron- and manganese-free water to be fed continuously during each test run to the adsorption columns in series. A bag filter unit was used to further protect the Ambersorb® 563 columns by removing residual solids that did not completely settle in the hold/decant tank. Sludge from the metals pretreatment stage was drummed after the pilot study for disposal as hazardous waste. A recycle line to the day tank allowed forward flow to be throttled to 0.5 gallons per minute (gpm). Water flowed upward through each column in series and treated effluent was then discharged to the sanitary sewer.

Figure 1 - Ambersorb® Treatment Train

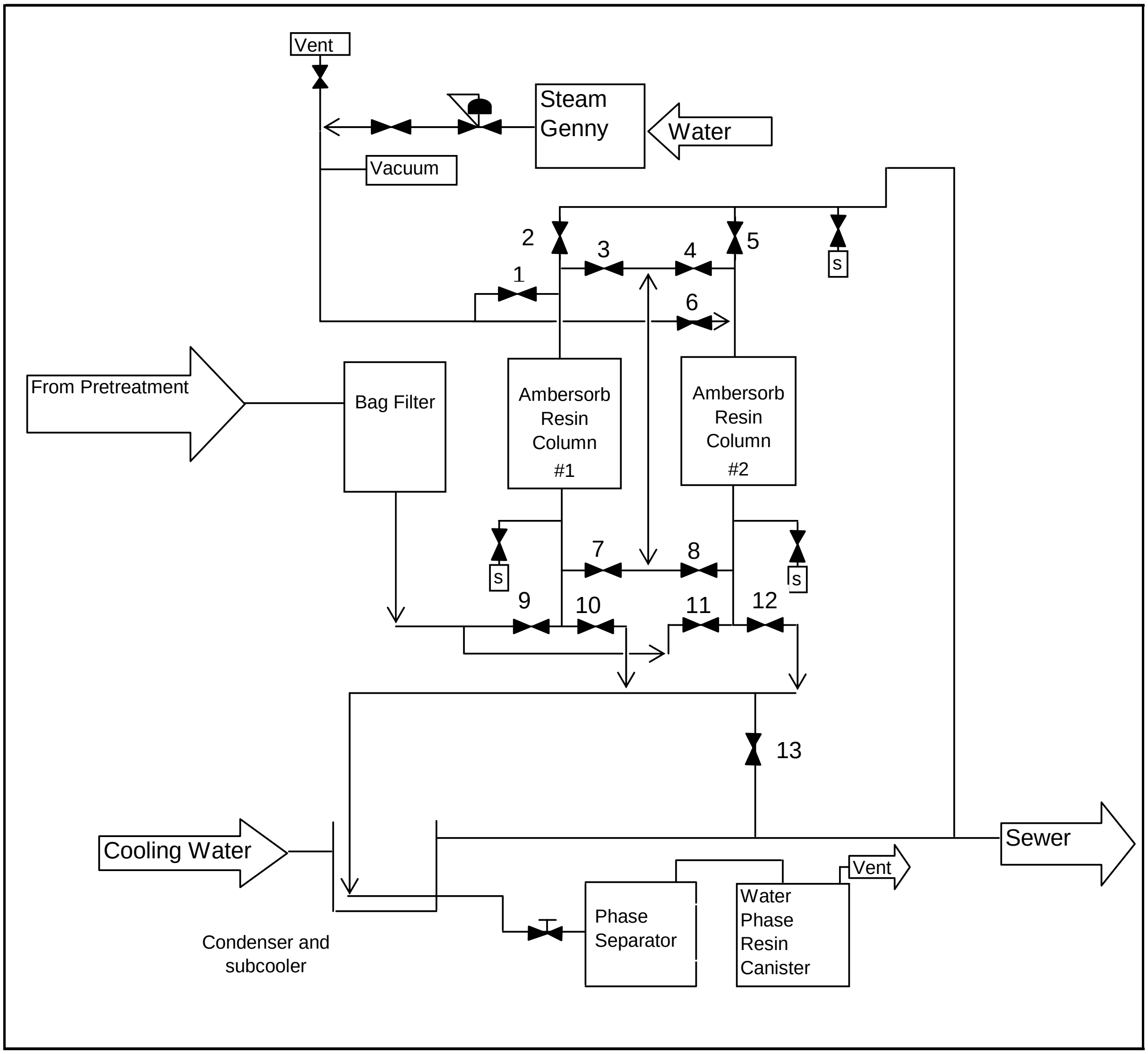


Table 1 – Historic Groundwater Characteristics

Iron, mg/L	2.4 to 16.0
Manganese, mg/L	0.28 to 0.69
1,1,2,2-TeCA, μg/L	1,940 to 2,400
TCE, μg/L	1,370 to 1,830
DCE, μg/L	360 to 530
VC, μg/L	37 to 60

For purposes of this pilot study, breakthrough was defined as any VOC concentration in the lead column effluent exceeding one-half its influent concentration. At breakthrough the lead column was regenerated using steam in accordance with the manufacturer's literature. Steam was directed downward through the spent resin column into the condenser coil. Condensed liquid was collected in the phase separator carboy, where the water and organic phases separated. Noncondensable vapors were vented through a canister of Ambersorb® 563 to prevent the escape of VOCs to the atmosphere.

Ambersorb® 563 Treatment

Eight pilot test runs were conducted at an Empty Bed Contact Time (EBCT) in each column of approximately 1 minute. Adsorption columns were operated in an upflow mode. The Ambersorb® 563 system operated continuously except during a metals precipitation pretreatment cycle, while a column was being regenerated, or when the VOC removal system had to be surged to remove elevated iron levels that may have passed through the bag filter.

Ambersorb® 563 Regeneration

Nine regeneration cycles were completed during the study. The final regeneration cycle at the end of the pilot study was a repeat of the previous regeneration to determine whether additional VOCs could be removed from the media by this procedure.

Based on previous Ambersorb® 563 treatability tests, it was expected that VC would define the media capacity and break through the lead column before the other influent VOCs. With the virgin media, breakthrough was estimated to occur after 5 days of operation (approximately 3,600 gallons of water treated), based upon groundwater characteristics shown in Table 1. Subsequent runs with regenerated media were expected to show breakthrough after 3 days of operation (approximately 2,300 gallons of water treated). Regeneration was accomplished using steam, initially at 34.5 psig, 280 °F, modified in some of the later regenerations to counter heat losses from the pilot units. Following regeneration, the system was returned to the forward flow treatment mode with the freshly regenerated column in the second-stage or lag position.

The small scale of the pilot test resulted in low condensate volumes from a single test run. In order to accurately measure the quantity of organic phase and obtain sufficient volume for analytical testing, the condensate was retained in the phase separator for several regeneration cycles to allow sufficient organic phase accumulation. Aqueous phase was decanted as necessary to provide sufficient volume in the collection vessel for the next regeneration cycle. The aqueous and organic phases were collected for disposal as hazardous waste.

Monitoring

Analytical monitoring had a threefold purpose for this study: (1) to aid in the proper operation of the pilot plant; (2) to verify that the treated water quality meets the performance levels established for the full-scale groundwater treatment plant; and (3) to support the determination of the Ambersorb® capacity to remove VOCs after multiple exhaustion and regeneration cycles. Samples were collected from the influent and effluent of the lead column, and effluent from the lag column, as shown in Figure 1. Samples were analyzed by EPA Method 8260 for 1,1,2,2-TeCA, tetrachloroethene, trichloroethylene, 1,2-dichloroethane, 1,1,2-trichloroethane, 1,1-DCE, chloroform, cis 1,2-DCE, trans 1,2-DCE, VC, carbon tetrachloride, bromodichloromethane, chlorobenzene, bromoform, dibromochloromethane, and benzene. Arsenic, iron, and manganese were analyzed periodically. In addition, the well influent and the aqueous and organic phases from regeneration were sampled. Routine iron tests were run with a field test kit on the influent to the Ambersorb® system. Analytical samples were sent to an off-site laboratory under chain-of-custody documentation for analysis. A 24-hour turnaround time was used for the first-stage effluent and trip blank samples to allow timely decisions regarding breakthrough. A 7-day turnaround time was used for the remaining samples collected.

PILOT TEST RESULTS

Table 2 summarizes results from the eight pilot test runs, including the volume of water treated in that run, the number of bed volumes (BV) treated, and major observations from the test data. The key analytical data defining performance of the Ambersorb® 563 resin are the breakthrough results of the lead column. These results are presented in graphical form for the final three operating runs in Figures 2, 3, and 4. Influent data for the entire study are presented as Figure 5. In addition to the data around the columns described above, two samples of well water were analyzed to assess potential loss of VOCs during pretreatment. The results suggest VOCs were lost during pretreatment, but ample levels remained for the resin adsorption pilot test.

The detection of TCE and VC during Run 3 is an unusual pattern for an adsorption column. A similar pattern was observed in Run 4. Typically, adsorption occurs at the influent end of the column and as this section becomes saturated the adsorption zone progresses toward the effluent end until breakthrough occurs, beginning at a low concentration and increasing until the effluent level approaches that of the influent. Adsorption is an equilibrium phenomenon such that saturation of the medium typically increases with increasing aqueous concentrations; previous testing by the manufacturer confirmed an isotherm type of equilibrium performance for this material (Parker and Bortko, 1991; Isacof et al., 1992; Parker, 1992). Lower influent concentrations may leach from a previously adsorbed contaminant's loaded column. The leakage of VOCs from the lead column in this and subsequent runs may represent residual TCE and VC left on the resin from the previous, possibly incomplete regeneration being flushed from the column. However, this column served as the second stage during Run 2 after it was regenerated. During that run there was leakage of a low concentration of VC, but no TCE. Since no samples

Table 2 – Summary of Pilot Test Runs

Run	Lead Column	Run Length		Results Summary
		Gallons	BV	
1	1	3078	5600	1. Run terminated at VC detection, below breakthrough criterion, in lead-column effluent. 2. No VOCs in second-column effluent.
2	2	3763	6830	1. Trace of TCE in lead-column effluent at startup. 2. VC detected during run in the second-stage column at a higher concentration (average 4.8 μg/L) than the first-stage effluent; believed to be the result of incomplete regeneration of this column after Run 1. 3. Run terminated by VC detection, below breakthrough criterion in lead column.
3	1	2484	4510	1. Run terminated by TCE/VC in lead column effluent at day 3, possibly from incomplete regeneration.
4	2	4400	7990	1. Similar pattern to Run 3; high TCE concentration in the first-stage effluent after 4 days, decreasing during the next 3 days. VC levels fluctuated as breakthrough progressed. 2. Run extended after detection of VC in lead-column effluent to observe breakthrough.
5	1	4202	7630	1. Some early leakage of TCE; initial levels were low. TCE leakage peaked approximately halfway through the run, followed by recovery. 2. VC was detected in the lead-column effluent at 2,980 BV processed. Concentration increased as the run continued, representing a normal pattern of breakthrough. 3. No VOCs broke through second-stage column.
6	2	7550	13610	1. Variable leakage in lead-column effluent. High TCE levels 1 day after startup, decreasing until weather-related shutdown (52 days), high again on restart. 2. Run extended to 7,500 gallons to observe breakthrough. 3. No VOCs detected in second-stage column effluent.
7	1	7400	13430	1. TCE and VC fluctuated in lead-column effluents. 2. VC exceeded breakthrough criteria (50%) at approximately 10,900 BV. Run extended to observe breakthrough performance.
8	2	8600	15610	1. Lead-column effluent TCE concentration after 1 day was 1,100 ppb, along with traces of other VOCs. Subsequent TCE levels generally low. 2. VC increased gradually. 3. Two VOCs were detected in the second-stage effluent during the run: TCE at 1.4 μg/L after the first day of VOC treatment and VC at 1.2 μg/L the last day of VOC treatment. 4. VC exceeded breakthrough criteria at approximately 10,900 BV; run extended to observe breakthrough performance.

1. All runs at EBCT = 1 minute

Figure 2 - Cycle 6 1E (Column 2 Primary)
Canal Creek Groundwater Treatment Pilot Plant
(01/11/00 to 03/20/00)

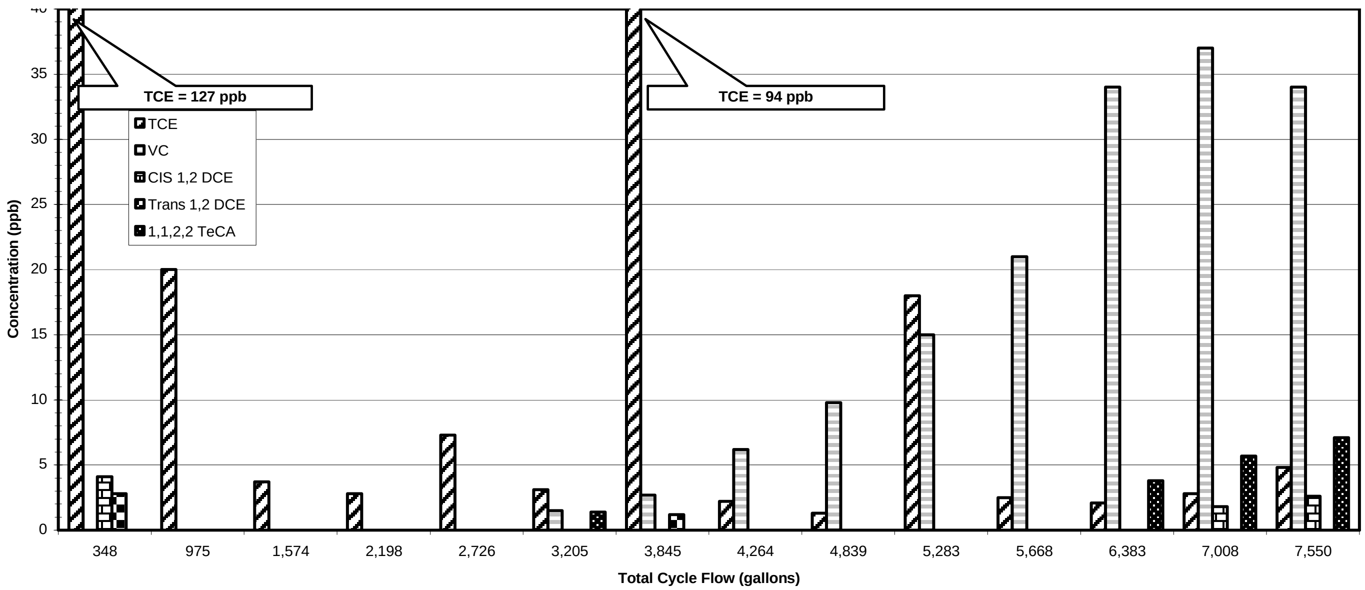


Figure 3 - Cycle 7 1E (Column 1 Primary)
Canal Creek Groundwater Treatment Pilot Plant
(03/20/00 to 04/04/00)

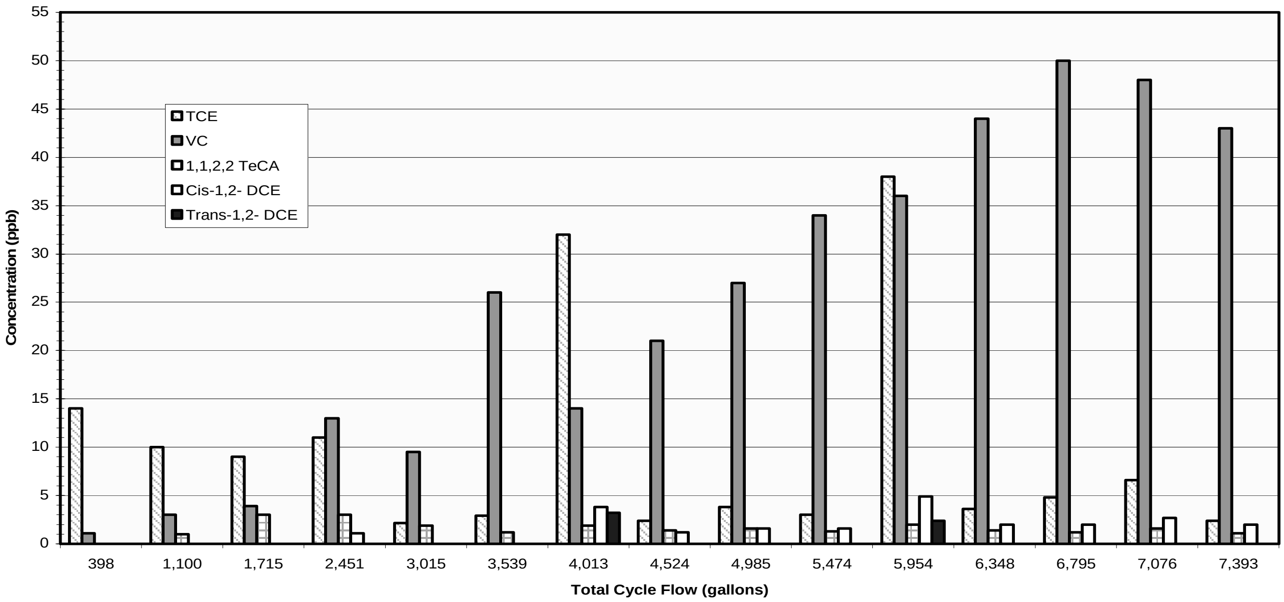


Figure 4 - Cycle 8 1E (Column 2 Primary)
Canal Creek Groundwater Treatment Pilot Plant
(04/04/00 to 05/03/00)

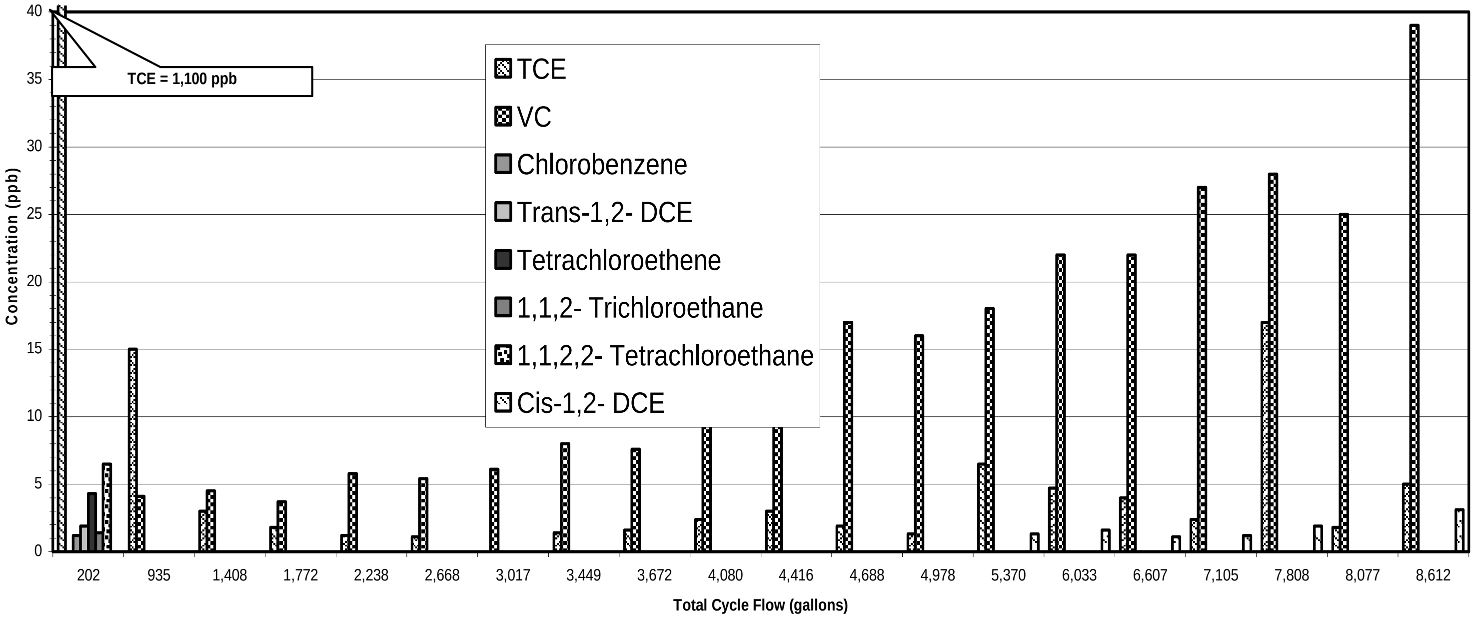
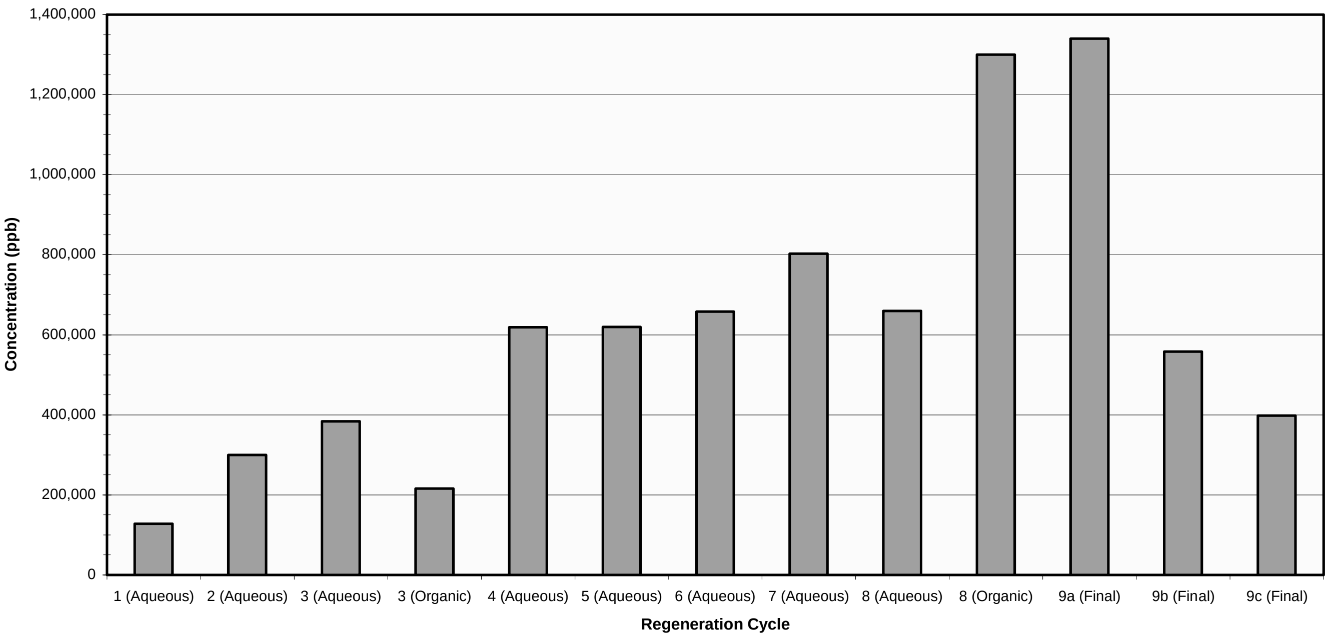


Figure 5 - Regeneration Sample Results for TCE
Canal Creek Groundwater Treatment Pilot Plant



were collected the first 2 days of the run, it is not known whether higher or lower levels were leaving the column during that period. A shutdown period, which occurred during some runs, may also allow contaminants to redistribute or migrate within the column and contribute to this breakthrough pattern. During normal operation in the upflow mode, the resin bed is lifted to the top of the column and held in place by forward flow velocity. Upon shutdown the resin bed falls to the bottom of the column. It is possible that upon restarting a partially exhausted column, the agitation causes some redistribution of the resin in the bed and the adsorption zone is disturbed. This is possible regardless of the duration of the shutdown. Regardless of leakage from the lead column, no VOCs were detected in the lag column effluent.

Run 5 results were unusual in that it would be expected that any high residual remaining after regeneration would have been released during the column's previous service as the second stage during Run 4 or from the beginning of Run 5 rather than during the run. The detection of TCE in lead-column effluent of Run 6 (Figure 2) was likewise unexpected since this column had been in service as the lag column for Run 5 with no breakthrough of VOCs. However, the level after the long shutdown may be more understandable assuming contaminants may also redistribute through diffusion.

Except for two elevated first-column TCE values, Run 7 results are considered normal performance for the system (Figure 3). VC was detected in low concentrations from the second-stage column on the last 3 days of Run 7. In an operating plant, this run would have ended at approximately 6,000 gallons (10,900 BV) after 11 days, when the first-column VC breakthrough was one-half the influent, thus precluding discharge of VC from the second stage. Run 8 was also extended (to 8,600 gallons) following lead-column breakthrough to observe the breakthrough (Figure 4). In an operating plant, this run would have been stopped at approximately 6,000 gallons (10,900 BV) when VC breakthrough concentration was one-half of the influent concentration. Overall the results of Runs 7 and 8 verify that VC breakthrough will control the life of the lead column and that effluent from the second column remains non-detect at the initial leakage of VC in the lead column, as would be expected.

Regeneration Cycles

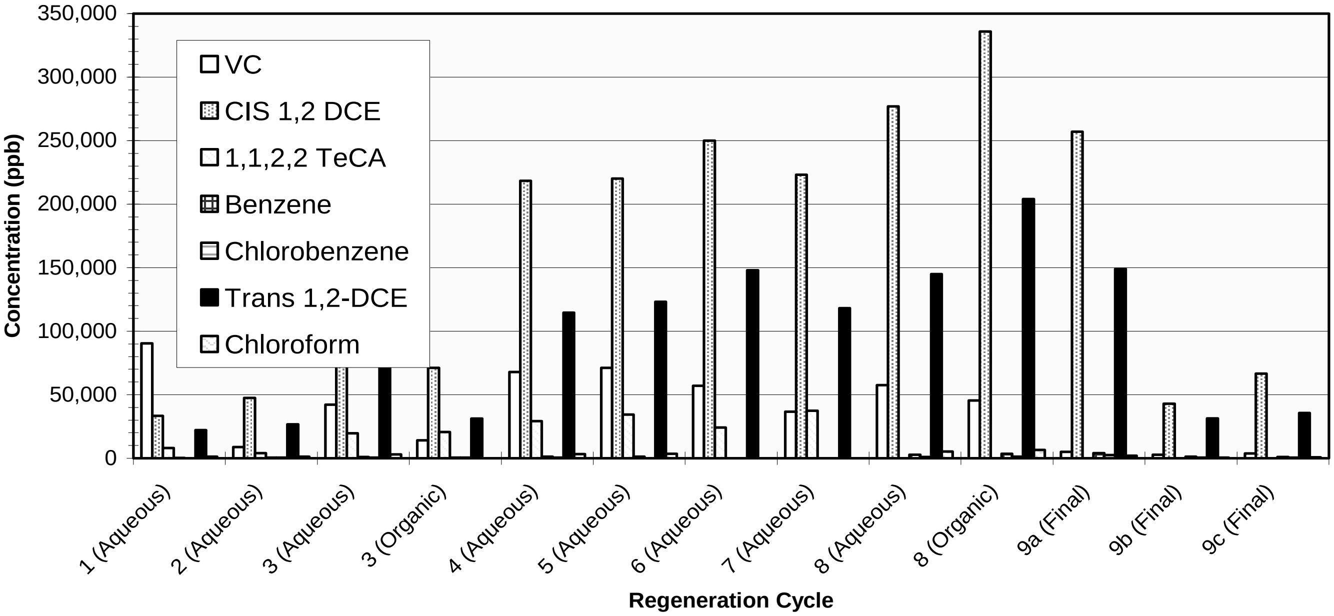
Analytical data from samples of regeneration condensate are summarized in Table 3 and presented graphically in Figures 5 and 6. Contaminants of concern detected in the influent groundwater were highly concentrated in the condensate. In addition several VOCs were detected in the condensate that were not detected in the influent samples, inferring their presence in the aquifer at levels below normal detection limits. It is possible that such constituents may over time affect the operating cycle of the plant. Acetone, for example, will not partition significantly to the organic phase in the phase separator and therefore will not be removed from the system when the organic phase is disposed of. Since it is not strippable it is also not removed in the plant headspace vapor control system. With extended operation it may prove useful to periodically dispose of the aqueous phase of the regenerant as well. This would constitute a small to moderate increase in total off-site disposal cost but does not fundamentally affect plant performance.

As discussed below, all of the regeneration cycles were incomplete based upon modest mass recovery and the observed pattern of individual VOCs leaking from regenerated columns placed

Table 3 – Analytical Data Summary for Regeneration Samples
Canal Creek Groundwater Treatment Pilot Plant
(analytical results in milligrams/L)

Regeneration	**1**	**2**	**3**	**3**	**4**	**5**	**6**	**7**	**8**	**8**	**9a**	**9b**	**9c**
Aqueous/Organic	Aque.	Aque.	Aque.	Org.	Aque.	Aque	Aque.	Aque.	Aque.	Org.	Mix	Mix	Mix
Acetone	0.15	ND	ND	ND	ND	ND	ND	ND	0.22	ND	0.21	ND	ND
Benzene	ND	0.55	0.45	0.45	1.4	1.3	ND	ND	2.7	3.4	4.0	1.2	1.1
Chlorobenzene	ND	0.44	0.43	0.43	0.54	ND	ND	ND	1.1	1.4	2.5	0.38	0.47
Dichlorobenzene	ND	ND	ND	ND	ND	ND	ND	ND	3.4	3.1	4.3	0.72	0.20
1,1-DCE	ND	ND	ND	ND	ND	2.47	7.80	ND	6.7	8.7	15.5	7.4	4.0
cis-1,2-DCE	33.5	47.6	7.2	7.2	218.2	220.1	250.0	223.0	277.0	336.0	257.0	42.9	66.6
trans-1,2-DCE	22.2	26.7	31.0	31.0	114.6	123.0	148.0	118.0	145.0	204.0	149.0	31.5	35.7
1,2-DCA	ND	ND	ND	ND	ND	ND	ND	ND	47.2	5.2	4.5	2.1	2.3
Ethylbenzene	ND	ND	ND	ND	ND	ND	ND	ND	1.2	0.92	3.0	ND	ND
Dichloromethane	ND	ND	ND	ND	ND	ND	ND	ND	24.9	25.7	28.2	87.0	10.4
Styrene	ND	ND	ND	ND	ND	ND	ND	ND	0.52	ND	ND	ND	ND
PCE	ND	ND	ND	ND	ND	ND	ND	ND	1.0	1.4	3.3	0.82	ND
Toluene	ND	ND	ND	ND	ND	ND	ND	ND	2.3	2.3	3.0	0.87	0.59
1,1,1-TCA	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.63	ND	ND
1,1,2-TCA	ND	3.4	5.2	3.9	12.1	13.1	19.2	22.2	15.6	25.1	26.2	11.9	11.3
TCE	127.8	300.1	383.5	215.7	619.2	620.0	658.0	803.0	660.0	1,300.0	1,340.0	558.0	398.0
Vinyl Chloride	90.3	8.9	42.3	14.0	67.8	71.2	57.0	36.8	57.6	45.4	5.1	2.7	3.7
Xylene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	10.10	ND	ND
Chloroform	1.2	1.2	3.1	ND	3.2	3.5	ND	ND	5.2	6.5	2.0	0.54	0.64
1,1,2,2-TeCA	8.0	4.1	19.5	20.6	29.2	34.3	24.0	37.4	ND	ND	ND	ND	ND

Figure 6 - Regeneration Sample Results for Other Contaminants of Concern
Canal Creek Groundwater Treatment Pilot Plant



back into service. To further confirm this, an extra regeneration cycle was performed at the end of the study to indicate the extent of additional VOC contaminants recoverable by additional steaming. Three samples were collected during this final regeneration: one was collected directly from the condensate line shortly after the start of regeneration, a second sample was collected in the middle of the final regeneration cycle also from the condensate line, and a third as a composite directly from the phase separator. All three samples included organic- and aqueous-phase liquids. These results show significant additional VOCs being removed from the column by additional regeneration, confirming that regeneration was not complete in the pilot unit.

There were two attempts to sample an organic layer from the phase separator, after Regenerations 3 and 8. After decanting most of the upper layer, the remaining condensate was transferred to a separatory funnel for separation. These samples were considered to be aqueous, but contained some visible solids. No organic layer was formed because the aqueous concentrations never reached the solubility limit. In full-scale operation, superloading can be used to help increase concentrations to saturation and produce a separate organic phase.

The concentration of TCE in the condensate increased significantly with each regeneration while other VOCs showed lesser increases. This was likely a result of increasing the pressure/temperature of the steam supplied to the column. The lower temperature resulted in an increased volume of condensate being generated per unit of VOCs removed. Table 3 shows the operating data for each regeneration. The initial target temperature within the column was 280° as 34.5 psig. Significant heat loss occurred from the small pilot-scale columns in spite of a layer of insulation. Inlet pressure was raised to 44 psig for regenerations 2 to 5 and to 61 psig for the remainder, corresponding to 308°F.

A preliminary mass balance was estimated for each regeneration using influent concentration data and flow volumes, with condensate concentration data. The loading to each column was calculated, taking into account loadings to the column resulting from the previous run, when that column was in the lag position. Each line in this table corresponds to an influent sample and the resulting concentration was applied to the incremental flow to that point to obtain the loading values. Calculated residual VOC levels left on each column from incomplete regeneration were added to the new loading to that column in the next run. Data, provided in Figure 7, indicate that even though the concentration of VOCs in the condensate increased with increasing pressure/temperature, the total mass recovered as condensate remains a fraction of the calculated loading. On average, approximately 40% of the calculated new loading was recovered in the condensate. Some of the remaining VOCs may have been in the vapor phase, which was not analyzed. However, the data also suggest potential increasing residual on the resin. Additional observation at full scale was recommended.

FULL-SCALE TREATMENT

Design

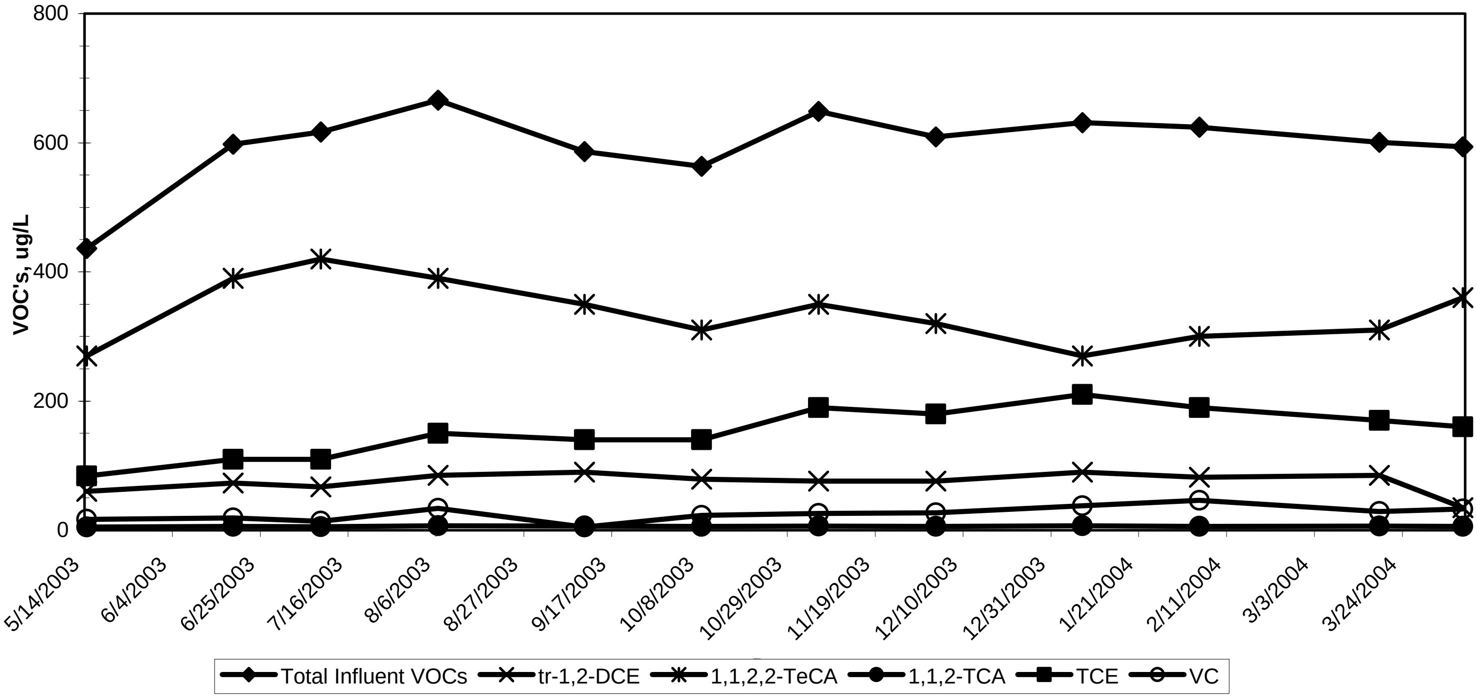
Full-scale design for the Canal Creek Groundwater Treatment Plant was based upon a groundwater flow rate of 440,000 gpd (305 gpm) with a maximum flow through the columns (including return streams) of 350 gpm. Influent VOC levels were established at one-half the historical maximum levels shown in Table 4, to allow for dilution of the static levels during continuous aquifer pumping.

Table 4 - Concentrations of Chemicals of Potential Concern in the East Canal Creek Area Plume

Chemical	Maximum Historical Concentration (µg/L)
Aldrin	0.06
Benzene	5.0
Bromodichloromethane	5.0
Bromoform	3.0
Carbon tetrachloride	13.0
Chlorobenzene	11.0
Chloroform	7.0
Dibromochloromethane	4.0
1,2-Dichloroethane	7.0
1,1-Dichloroethene	6.0
1,2-Dichloroethene (total)[1]	1,400
1,4-Oxathiane	0.860
1,1,2,2-Tetrachloroethane[1]	1,900
Tetrachloroethylene	7.0
1,1,2-Trichloroethane	25.0
Trichloroethane[1]	1,600
Vinyl Chloride[1]	130
Arsenic	56.1
Iron[1]	30,600
Manganese[1]	2,560

Note 1: Parameters used as the design basis for chemical removal.

Figure 7 - Plant Influent VOCs



For the original Canal Creek Groundwater Treatment Plant 30% Design (Weston, 1999b), prior to this pilot testing, resin capacity at breakthrough was estimated at 0.011 lb of VC per cubic foot of media. This value reflected the loading of 0.017 lb/ft^3 from the initial testing (PNL, 1998) and an allowance for reduced capacity following regeneration as observed in the SITE demonstration testing (Weston, 1995) using adsorption columns 5 feet in diameter and 4 feet resin bed depth each 78.5 cubic feet). This loading resulted in a predicted regeneration cycle of 6 days at the VC concentration of 65 μg/L used as a design basis.

As noted above, pilot test Runs 6, 7, and 8 were extended beyond the defined breakthrough concentration (one-half the influent concentration) to observe breakthrough. Based upon that criterion, these runs would normally have terminated at approximately 6,000 gallons (10,900 BV) treated. The VC loadings at the breakthrough point and average influent VC concentrations were as follows:

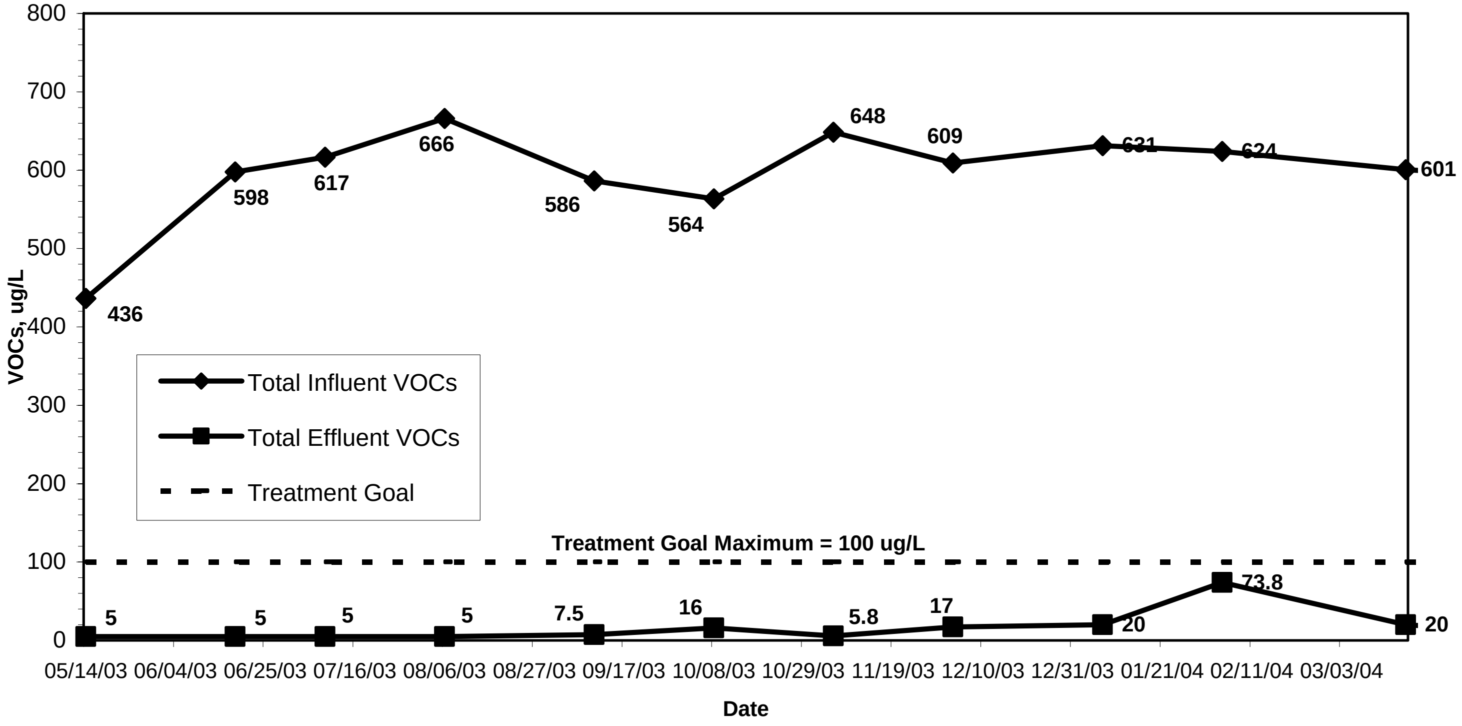
• Run 6	0.051 lb/ft^3	102 μg/L
• Run 7	0.053 lb/ft^3	106 μg/L
• Run 8	0.027 lb/ft^3	55 μg/L

These results indicated, as expected, that loading capacity is proportional to the influent concentration. Therefore, at the design basis of 65 μg/L the loading capacity was interpolated to be 0.032 lb/ft, significantly higher than the estimated values for the preliminary design. Groundwater treatment capacity at this concentration could be approximated as 60,000 gallon/ft^3 of resin to the defined breakthrough because 6,000 gallons were treated by 0.1 ft^3 of media in the pilot study. A design EBCT of 3.4 minutes and a surface loading rate of 8.9 gpm/ft^2 (at the maximum flow of 350 gpm) were retained for full-scale design to provide a highly conservative bed volume and life and to reduce headloss in the columns. Using these values for the full-scale plant at 440,000 gpd, and 160 ft^3 of media per train, 9.6 million gallons would be treated per run and regeneration of two lead columns required every 22 days. These results enhance the design and operating parameters for the full-scale system as compared to the pretesting estimates, with reductions in operation and maintenance costs. It should be noted that even with these conservative loadings, the size of the adsorption columns (four columns, each 5 ft diameter, 6 ft total height with 4-ft resin bed depth) were significantly lower than with comparable adsorption technologies such as granular activated carbon (GAC), which typically used EBCTs on the order of 15 to 20 minutes.

Operation

Based upon these design criteria the full-scale plant was constructed and began operation in April 2003. Routine operation at 288,000 gpd began in 30 April 2003 (with the remainder of the 440,000-gpd capacity being in reserve for future expansion). In the first year of operation approximately 71 million gallons of contaminated groundwater were treated with all effluent VOCs meeting expected performance levels. Average total VOC removal efficiency during that time was 96%. Figure 8 shows influent and effluent data for the first year as compared to the surface discharge criterion of 100 ppb total VOCs. These results clearly demonstrate that full-scale treatment will provide effective performance in terms of effluent quality. During the startup period, many of the regeneration events were initiated not by contaminant breakthrough but in the course of other operational adjustments and fine tuning of the plant. Therefore the data to

Figure 8 - Canal Creek GWTF – Total VOCs
May 2003 – March 2004



date do not allow complete verification of the predicted service life of the bed. Long-term operating experience will further predict the performance of the resin. Multiple regeneration cycles to date do not provide clear evidence of any decline in resin performance. Field observations did raise the question of potential resin loss by attrition. The design included an allowance for 10% resin replacement per year for attrition and/or reduction in capacity. As discussed previously, most regenerations during the initial operating period were dictated by operational requirements not related to VOC breakthrough, including, in particular, observed pressure drop increase across the columns. Early experience and inspection of the adsorption columns indicated a tendency for fine particles to accumulate in column outlet header screens, suggesting attrition by fining or possibly a problem with the header configuration. In order to evaluate the possibility of resin attrition, samples of virgin resin and used resin from various bed depths were analyzed by particle size analysis, nitrogen porosimetry, and photographic visualization. The results are shown in Figure 9. Although particle size analysis indicates some fining, the interpretation is complicated by the possible presence of other fine solids (e.g., fine metals precipitates), which are not distinguishable by sieve analysis. To date, these changes in resin condition do not affect the performance of the system. Long-term experience will likewise allow quantification of the actual attrition rate for better prediction of operating requirements and cost for resin replacement.

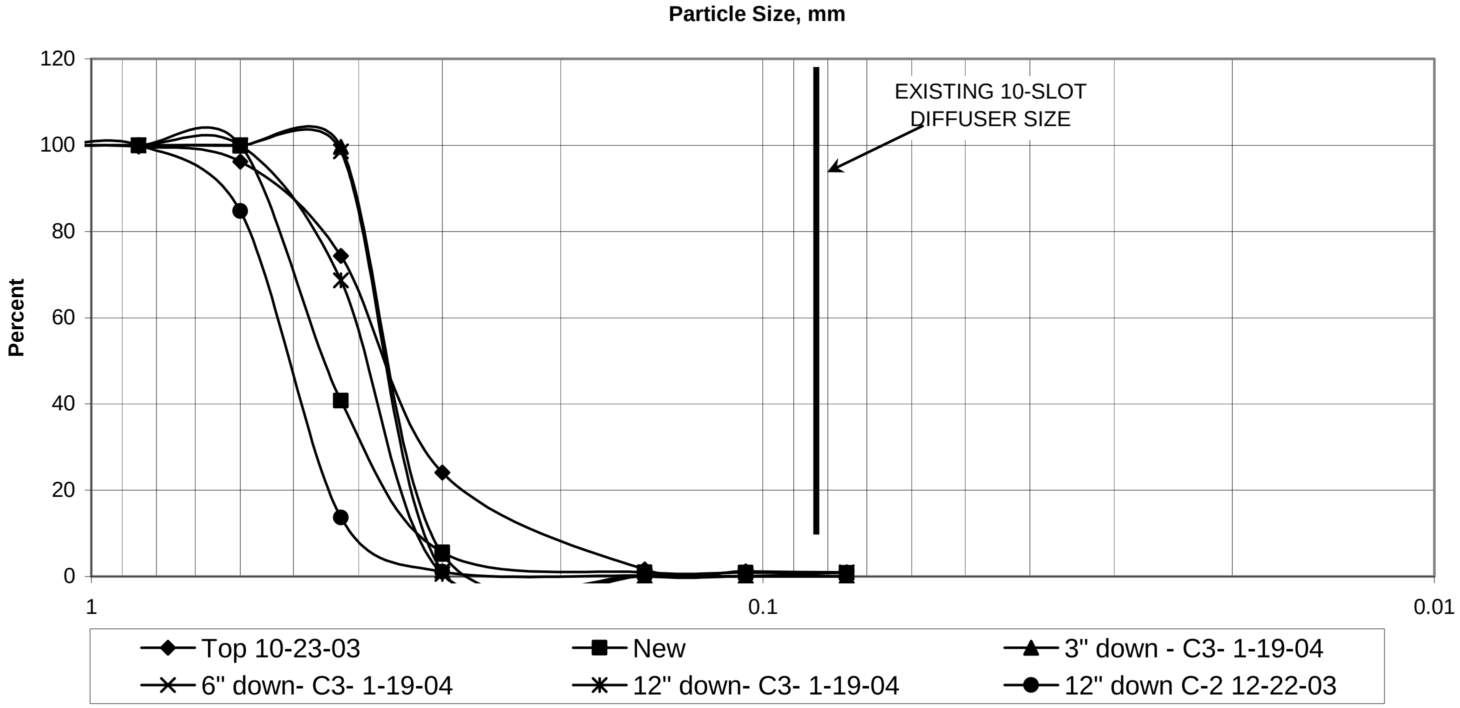
CONCLUSIONS

Overall, the pilot study has confirmed the effectiveness of Ambersorb® 563 in removing VOCs from the groundwater to non-detectable levels. The results of the pilot test confirm that resin adsorption can provide high-quality effluent even at very low EBCT values and after multiple regeneration steps. It was found that at the start of some test runs, some unexpected initial VOC leakage occurred. Based upon available information, this leakage is related to incomplete regeneration and to some extent may be an artifact of the small-scale pilot test configuration. It was found that increasing temperature and in one case repeating the regeneration process increased recovery of VOCs from the resin, supporting this inference. Although such problems are not expected to be a major factor in full-scale application, additional investigation into the optimal regeneration approach is warranted to further optimize performance of the system. At the levels of these tests and in light of the lead-lag mode of operation, these issues did not affect the final effluent quality.

The pilot study results confirm that VC is the controlling parameter in defining the adsorptive capacity of the Ambersorb® 563 media. Generally, VOCs were not detected in the final effluent. The few isolated samples with positive results were at trace levels and were due to incomplete regeneration after Run 1, or allowing the run to continue beyond the normal end point in the case of Runs 7 and 8.

Pilot study regeneration cycles were incomplete and are attributed to heat losses from the small pilot-scale columns reducing the temperature within the bed. This was not expected to be a problem with the full-scale design because the columns are better insulated and the larger columns have much less surface area per unit of volume. The study did not yield data on partitioning among the three phases due to the small scale of the operation and the low quantity of contaminants available for samples. The total quantity of aqueous phase condensate from each

Figure 9 – Ambersorb® Resin Particle Distribution (mm)



regeneration cycle was approximately 2.2 gallons, while the estimated organic phase was only 36 grams.

The results of the pilot study demonstrate that with proper control of the service run and regeneration of the media, Ambersorb® 563 will produce water containing no detectable VOCs. The volumetric loading capacity demonstrated by the pilot test will allow a 22-day service run after each regeneration. The mass loading capacity was found to be proportional to the influent VC concentration, thus resulting in a fixed volumetric capacity over the range of expected VC levels.

In summary the pilot test validated the performance of synthetic resin adsorption for this application and provided data for design. More than 11 months (to date) of full-scale operating experience further validates the performance of the resin in terms of effluent quality. Longer term observation and analysis should be used to further quantify and validate operating parameters in terms of regeneration efficiency and resin life.

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