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Treatability Testing Report

# REMEDIAL CLEANUP TREATABILiTY STUDY MILLCREEK SUPERFUND SITE ERIE, PENNSYLVANIA

U.S. Army Corps of Engineers Omaha District

July 1989 Project: 0285-23-1



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MILLCREEK SUPERFUND SITE ERIE COUNTY, PENNSYLVANIA

Prepared By:

MALCOLM PIRNIE, INC.

for the

U. S. ARMY CORPS OF ENGINEERS OMAHA DISTRICT

JULY 1989

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PIRNIE MALCOLM PIRNIE, INC. ENVIRONMENTAL ENGINEERS, SCIENTISTS & PLANNERS



August 9, 1989

U.S. Army Corps of Engineers 215 North 17th Street Omaha, Nebraska 68102

Attention: Captain Christopher J. Young (CEMRO-ED-EC)

Re: Mi 11 creek Superfund Site Treatability Testing Report

Gentlemen:

Malcolm Pirnie, Inc. is pleased to submit this final Treatability Testing Report. Our responses to your specific comments (received April 14, 1989) to the draft Treatability Testing Report (February 1989) are incorporated by reference into this final report and are enumerated in Appendix C. The Treatability Testing Report will remain as a stand-alone report, documenting the procedures and results of the treatability tests performed for this study. The recommendations for a ground water treatment system with associated capital and operating costs are discussed in the Engineering Report. Where appropriate, the responses to comments have also been incorporated into the Engineering Report.

Should you have any questions or comments, please contact us.

Very truly yours,

MALCOLM PIRNIE, INC.

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Dharmarajan R. Iyer, Ph.D. Project Manager

ms/DRI08099.L

c: Mr. Tony Koller, USEPA Mr. Mark German, PADER Mr. Paul Werthman, MPI Mr. Douglas Daley, MPI

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1.0 INTRODUCTION

1.1 BACKGROUND

The U.S. Army Corps of Engineers (COE) retained Malcolm Pirnie to conduct a Remedial Cleanup Treatability Study at the Millcreek Superfund Site in Erie, Pennsylvania. The objectives of this study were to define the extent of volatile organic contamination of the shallow aquifer, to determine hydraulic characteristics of the aquifer in order to estimate flow rates for remedial action, to model contaminant transport in the soil and ground water, and to evaluate ground water treatment alternatives. These objectives were to be achieved through a combination of field investigation, computer modeling, laboratory analysis and pilot scale studies. Malcolm Pirnie prepared a Work Plan to define the level of effort necessary for the planned project activities. The scope of the Work Plan was based upon information obtained during a Remedial Investigation (RI) in 1985 and previous studies in 1982 by the U.S. Environmental Protection Agency (EPA) and the State of Pennsylvania Department of Environmental Resources (PADER).

A field investigation by Malcolm Pirnie was intended to supplement information obtained during the previous RI and to collect additional information for use during design and remediation. The planned field investigation activities included:

- soil boring and sampling;
- soil column leaching test;
- monitoring well installation;
- pumping and observation well installation;
- 72-hour pumping test;
- ground water sampling; and
- treatability testing.

Except for the 72-hour pump test and the ground water treatability testing, the field activities were completed between April 25 and June 28, 1988. The pump test was postponed due to the inability of the newly-installed pumping well to sustain a yield greater than one gallon per minute (gpm). As the treatability testing was to be performed on contaminated ground water obtained from the pumping well located in the ground water contaminant plume defined in the RI, the treatability testing

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was postponed until the analytical results of the soil and ground water sampling were reviewed and evaluated. This report describes the procedures and equipment used for bench- and pilot-scale testing performed between September 28 and October 19, 1988 at the Millcreek site. The recommendations for a groundwater treatment system and associated capital and operating costs are included in the Engineering Report (August 1989) for the Remedial Clean-up Treatability Study.

#### 1.2 PURPOSE AND SCOPE

The purpose of the treatability testing was to provide sufficient information for the design of a ground water treatment system. This treatability testing is one aspect of the overall treatability study and design process. The treatability study addressed the following:

- Establishment of effluent discharge criteria;
- Bench and pilot testing for organics and inorganics removal;
- Evaluation of alternate treatment methods;
- Selection of a recommended treatment scheme;
- Development of design criteria; and
- Preparation of preliminary capital and operating costs.

The treatability testing included the following:

- an air-stripping pilot study using ground water pumped from monitoring wells MW-9 and MW-10;
- bench-scale testing for inorganics removal on representative ground water samples before and after air-stripping;
- testing of activated carbon for organic contaminant removal; and
- sludge dewatering and disposal methods.

A field office was set up at the site and supplied with all equipment necessary to conduct the testing. Samples for chemical analysis were either hand-delivered or shipped by overnight delivery to Recra Environmental, Inc., Amherst, New York.

### 1.3 GROUND WATER DISCHARGE CRITERIA

The Record of Decision issued by the USEPA did not specify discharge/ clean-up levels for the contaminants of concern in the ground water at the Millcreek site. However, the USEPA, Region III conducted an assessment of the ground water treatment system and recommended (December 16, 1987 letter to the U.S. Army Corps of Engineers) the following criteria regarding the clean-up of the ground water and the discharge of treated ground water to Marshall's Run. Based on these recommendations, the following design parameters were selected:



The effluent criteria for discharge of treated ground water to Marshall's Run were recommended by the USEPA based on the Safe Drinking Water Act (SDWA), Clean Water Act (CWA) and the Pennsylvania Chapter 93 Water Quality Standards. There are currently no State and Federally regulated effluent limits for 1,1-Dichloroethane and 1,2-Dichloroethene, which are two other volatile organics of concern at the Millcreek Site. As 1,2-DCE was detected consistently in all ground water samples during this testing, a design effluent limit of 70 ug/1 is used to assess the air stripping system. Effluent criteria specified above were used to develop the basis of design for the ground water treatment system. The design influent concentrations are based on the concentrations observed in ground water samples during the 1985 RI/FS and this field investigation.

Alternatives to ground water treatment and discharge to the creek include discharge to the City of Erie Wastewater Treatment Plant (WWTP) with or without treatment of the ground water. The City of Erie ordinance

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23-1984 regulates the discharge of waste into the public sanitary sewerage system. Restrictions are placed on total metals (sewer discharge limit of 25 mg/1 for iron), phenolics (15 mg/1 discharge limit), phosphates (15 mg/1), and oil and grease (100 mg/1). Generally, the maximum concentrations of the total metals detected in individual water samples from the site are less than the maximum allowable concentrations under the Ordinance (see Appendix A). There are no specific discharge limits on volatile organic contaminants.

The WWTP has a design flow capacity of 68.6 MGD, with average daily flow presently between 35 and 45 MGD, and a peak daily flow of 58 MGD. The major industrial wastewater flow is from a paper manufacturing facility at 15 MGD. In addition, the City receives leachate from a nearby sanitary landfill. In a joint meeting between the USEPA, City of Erie and Malcolm Pirnie (May 1989), the City indicated that the sewer capacity adjacent to the Millcreek site and the hydraulic capacity of the wastewater treatment plant were limited. In addition, the City was concerned about the potential risk of exposing the public to VOCs should untreated ground water be discharged to the sanitary sewers. Even though the City has no discharge limits for VOCs, the City wanted the ground water treated for organics prior to discharge to the sewers.

## 2.0 GROUND WATER CHARACTERIZATION

The treatability testing was performed on ground water pumped from wells located in the area of the contamination plume under the eastern portion of the site. Six monitoring wells (MW-2, MW-5, MW-9, MW-10, MW-33B, OW-1) as shown on Sheet 1 were initially selected to provide water for testing. These wells were selected because of the'presence of elevated concentrations of VOCs in the ground water and because each well could potentially sustain a pumping rate greater than one gallon per minute (gpm) based upon the hydraulic conductivity testing results.

Prior to commencing the air-stripping test, each monitoring well was pumped to determine whether it would yield a sufficient amount of water for testing. Wells MW-33B, MW-2, MW-5 and OW-1 were evacuated within several minutes when pumped at one gpm. It was apparent that these wells

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could not be used to provide the sustained flows needed for the treatability testing. Monitoring wells MW-9 and MW-10, which were capable of sustaining yields of approximately eight and six gpm, respectively, were pumped simultaneously to provide the water needed for the airstripping and other treatability testing.

Water level measurements taken at various times during the treatability testing are included in Table 1 in terms of elevations and depth below ground surface. The static water levels in wells MW-9 and MW-10 were measured prior to pumping each well. In addition, water levels in these two wells were periodically measured during pumping to monitor the drawdown. The water levels in wells MW-2, MW-5, MW-23A, MW-23B, MW-33A, MW-33B, MW-34, PW and OW-1 were periodically measured when pumping wells MW-9 and MW-10 for treatment.

For flows ranging between 5.4 and 6.0 gpm, the total drawdown in MW-10 ranged from 2.39 to 3.25 feet. The well was capable of sustaining a pumping rate of 6 gpm for time periods of up to 6.5 hours. On one occasion when the pumping rate was increased to 6.6 gpm, the drawdown increased an additional 0.95 feet (total drawdown of 4.69 feet) within five minutes. The drawdown in MW-9 ranged from 0.34 to 0.50 feet for flows between 6.6 and 7.6 gpm. On one occasion when the pumping rate was increased to 10.0 gpm, the water level dropped 0.02 feet after one hour. At the conclusion of the field testing, the flow meters indicated that a total of 32,775 gallons and 21,820 gallons had been withdrawn from monitoring wells MW-9 and MW-10, respectively, throughout the duration of the field'testing.

Water levels in the observation well (OW-1) and pumping well (PW) located approximately 120 feet away from MW-9 decreased between 0.04 and 0.07 feet while pumping MW-9. No appreciable changes were "noted in the water levels in MW-23A and MW-23B while pumping MW-10. Since the wells were not pumped for more than 12 hours, the influence of long-term pumping of MW-10 and MW-9 was not determined.

The influence of precipitation on the water levels appears to be more pronounced than pumping ground water. Total daily precipitation is listed in Table 2. Generally, the water level elevations increased in all wells over the time of testing. This is probably due to precipitation,

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which totalled 3.82 inches for the two-week period of testing. The static water levels in MW-9 and MW-10 increased 1.08 feet and 1.02 feet, respectively, between October 1 and 12. This increase could be attributed to the 1.75 inches of precipitation recorded on October 9 and 10.

Untreated water samples were analyzed prior to each phase of the testing to provide a basis of comparison. The ground water quality is described in each section. Since water quality samples collected during the testing were intended for use in evaluating treatment techniques only, external quality control (QC) samples were not required. Internal QC samples were analyzed in accordance with laboratory protocols.

### 3.0 VOLATILE ORGANICS REMOVAL BY AIR-STRIPPING

3.1 PURPOSE

Pilot scale testing was performed to evaluate the use of a packed air-stripping column to remove volatile organic chemicals (VOCs) from contaminated ground water at the site. The following information was to be collected during the treatability testing:

> - determine if noxious off-gases from the air stripper need to be treated;

- evaluate the effect of air-to-water ratio on removal efficiency;

- - confirm the mass transfer efficiency of a selected packing material:
- identify any potential slugging or fouling problem.

The scope of the pilot study includes:

- operation of the pilot treatment system using different combinations of air-to-water ratios (A:W) and liquid loadings for a total of 10 trials;
- preparation of a preliminary design of an air-stripping system using both computer simulations and data obtained from the pilot-scale testing.

## 3.2 DESCRIPTION OF PILOT AIR-STRIPPER

The pilot air-stripping column, as illustrated in Figure 1, consisted of PVC influent piping and valve, 12-inch I.D. PVC column, packing media, air blowers and a support structure. Raw ground water was supplied from one of two sources: direct from the wells or from a 6500 gallon tanker truck used as a temporary storage tank. An electric booster pump was used to pump water to the top of the column. The flow rate was regulated with a globe valve and measured using a rotameter with a range of 5 to 40 gpm. Counter-current air flow was provided through a blower equipped with a metering valve and pressure gauge. Air was blown into the bottom of the column, up through the packing and out into the atmosphere. The air outlet was equipped with a mist eliminator. Effluent from the pilot column flowed by gravity through a 3-inch flexible hose with a trap and a 2-inch rubber hose into a temporary holding basin, from which it was pumped to the on-site pond.

An orifice-type liquid distributor was used to distribute the water at the top of the column and to allow air flow out the top of the column. The overall column height was 13-feet, while the packing height was 10-feet. The packing material used was 2-inch diameter Jaeger No. 1 Tri-Packs, a hollow, spherical-shaped packing of injection-molded plastic. Sampling taps were provided on the influent line after the pump and on the effluent line before the trap.

#### 3.3 TEST PROCEDURES

The testing consisted of 10 runs over a two week period at liquid loading rates ranging from 19.1 gpm/sf to 38.2 gpm/sf and air-to-water (A:W) ratios between 20:1 and 50:1. During the course of the air-stripper column runs, air-stripper effluent samples were also collected for activated carbon and inorganic removal testing. For each trial run, the desired A:W ratio and liquid loading rate were first obtained. The liquid flow rate was adjusted with the globe valve to attain the desired flow. The airflow was determined from measuring the air inlet pressure and referring to the blower curves. The airflow rate was adjusted using a



globe valve. The column was then operated for a two-hour time period thereby providing sufficient time for equilibration. Air-stripper influent and effluent (air-stripped) water samples were collected at 15, 60 and 120 minutes after the test had begun. At the time of sampling, the air and water flow rates and temperatures were recorded. A summary of the test conditions is presented in Table 3. For all the trial runs except Trial 10, the ground water was temporarily stored in a 6500-gallon stainless-steel tank, and then pumped to the tower when a sufficient volume had been stored for a two-hour run time at the desired flow rate. For Trial 10, water was pumped directly from the wells to a 35-gallon equalization basin and then to the top of the tower. The ambient air temperature ranged from a high of 17'C to a low of 4°C during the testing runs. Influent (raw) ground water temperatures ranged from 12°C to 18.9'C, with an average of 14.3°C. This variation in the air-stripper influent temperature is largely due to the storage of ground water in the tank during testing. Actual ground temperature is generally uniform (less than 2'C variation) throughout the year.

#### 3.4 SAMPLING PROCEDURES

Influent (raw) and effluent (air-stripped) water samples were collected for VOC analysis during each of the 10 trial runs. In addition, a VOC sample was collected from a tankful of stored water to determine if short-term VOC storage had any effect on the ground water quality. When collecting water samples, each sampling port was slowly opened and allowed to flow to a waste bucket for 15-20 seconds. The VOC samples were collected in 40 ml vials, which were stored on ice after collection. Samples were shipped to Recra Environmental laboratory in Amherst, New York within 24 hours. Since the samples collected during this treatability testing were used for an evaluation of treatment techniques only and not for characterization of ground water, quality control samples were not required.

Discrete influent and effluent samples were collected at 15, 60 and 120 minutes after the start of each test run to ensure that steady state conditions were achieved. For Trial Runs 1, 2, 5 and 6, these three

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discrete samples were composited by Recra Environmental in their lab and analyzed as a composite sample. Only one discrete 60-minute sample for both influent and effluent from Trial Run 3 was submitted for analysis, while, for Trial Runs 4, 7, 8, 9, and 10, only discrete influent and effluent samples collected 120 minutes after startup were analyzed.

The empty bed contact times in the pilot air-stripping column were approximately 2 and 4 minutes at the minimum and maximum applied ground water flow rates of 15 and 30 gpm. Based on these contact times and Malcolm Pirnie's experience with pilot air-stripping columns, equilibrium conditions should be attained within 15 minutes of the startup of the column. Samples collected at least 15 minutes after the start of each run are therefore representative of the VOC removal efficiencies under the specific set of test conditions.

The samples for VOC analysis were initially composited at the analytical laboratory from grab samples taken at 15, 60 and 120 minutes after the start of each test run, in accordance with the Work Plan. The three discrete VOC samples for each run (influent and effluent) were submitted to the lab in 40 ml-vials. Equal aliquots from of three vials were withdrawn into a syringe until the desired total volume needed for the analysis was obtained. The syringe and purge vessel acted to mix the three discrete aliquots to obtain a composite VOC analysis. The purge time was sufficiently long (11 minutes) to allow any VOCs present to be purged to the GC/MS system. Due to the concerns over the loss of volatile organics during the compositing of samples and any error that may be introduced in the mass transfer calculations resulting from the averaging of concentrations, the procedure was modified in the field to analyze only discrete samples.

A review of the analytical data, summarized in Table 4, indicates little difference in water quality between discrete and composited influent samples. For 1,2 DCE, the influent composite samples ranged from 200 to 1300 ug/1, while the discrete samples ranged from 630 to 1200 ug/1. Similarly, TCE ranged from 9 to 15 ug/1 for composite influent samples, and from 11 to 12 for discrete influent samples. These results indicate that neither the fact that samples were composited nor the different time

intervals used for sampling (e.g. 15, 60 or 120 minutes) apparently affected the water quality.

## 3.5 RESULTS AND DISCUSSION

Five VOCs were consistently detected in the influent (raw) ground water samples at concentrations greater than the detection limit as shown on Table 4. These VOCs were:



The remainder of the VOCs listed in Table 4 were detected in various samples at less than the quantitation limit and are, therefore, presented as estimated values. The presence of methylene chloride in four untreated water samples may have been due to laboratory contamination. Only 1,2-DCE was detected in each air-stripped sample at concentrations sufficient for determining the efficiency of the air-stripping tower. While the remainder of the VOCs were removed to effluent concentrations at or below the laboratory detection limit (5 ug/1), the estimated concentrations were also used to determine the design criteria.

Because only wells MW-9 and MW-10 were used for the air stripping test, it is possible that VOCs not detected during the testing may be present in ground water collected during site remediation. Therefore, based on the VOC concentrations detected in the ground water during previous investigations, 1,2-dichloroethene, 1,1,1-trichloroethane, trichloroethene and vinyl chloride were selected for the air stripper evaluation and design calculations. The design influent concentrations and required removal efficiencies are given in Section 1.3.

Since 1,1-DCE was not detected in the ground water used in the pilot testing, there were no data which could be used to determine the mass transfer coefficient. However, as the Henry's Law constant for 0285-23-1125 -10-

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1,1-DCE is greater than the Henry's Law constants for 1,1,1-TCA, TCE, and 1,2-DCE, any system designed to remove the three compounds with higher Henry's Law constants should also adequately remove 1,1-DCE. In addition, the maximum 1,1-DCE concentration detected at the site during previous ground water sampling was 16 ug/1; only a 56% reduction is required to achieve the desired discharge concentration of 7 ug/1 for 1,1-DCE.

## 3.5.1 Mass Transfer Relationships

For each VOC of concern, a mass transfer coefficient  $(K, a)$  was calculated using the liquid flow rate, A:W ratio and the water temperature during each run. The data were then evaluated using linear regression analysis. A plot of the mass transfer coefficient for each VOC of concern as a function of the liquid loading rate is presented in Figures 2a through 2d. The variability in the calculated  $K_i$  a values from pilot data is largely due to experimental error rather than due to the variability in influent water temperature.

Based upon the relationship between the mass transfer coefficient and liquid loading rate, as well as the desired effluent concentration, the optimum liquid loading rate was determined. Malcolm Pirnie's experience with similar waters containing VOCs has demonstrated that a liquid loading of 30 gpm/sf provides optimum removal efficiency. Generally, the cost of treatment increases rapidly at loading rates less than 30 gpm/sf, but does not change significantly at loading rates greater than 30 gpm/sf. At a loading of 30 gpm/sf, the selected  $K_i$  a values would be:



The above values of  $K_i$  a obtained from linear interpolation of pilot data are consistent with values reported in the literature and Malcolm Pirnie's experience with similar packing material at other sites. Using these  $K_i$  a values at the desired loading rate of 30 gpm/sf and the desired removal

rates, a relationship between packing height and A:W ratio was developed for each VOC.

3.5.2 A;W Ratio

For each desired VOC removal efficiency, the relationship between packing height and the A:W ratio at a liquid loading rate of 30 gpm/sf is illustrated in Figure 3. Henry's Law constants for column sizing are based on the lowest reported influent water temperature. Increasing the A:W ratio from 10:1 to 40:1 results in a significant reduction in packing height, particularly for removing 1,2-DCE. Beyond an A:W ratio of 60:1, the reduction in packing height associated with an incremental increase in A:W ratio is minimal. The removal of vinyl chloride is unaffected by changes in the A:W ratio; however, a packing height of 22 feet is required to achieve the desired 99% removal rates. Both TCE and 1,1,1-TCA are effectively removed at packing heights less than 22 feet.

Selecting both 1,2-DCE and vinyl chloride as the critical design compounds indicates that, for a 22-foot packing height, a minimum A:W ratio of 40:1 is required for meeting removal requirements. To ensure that a sufficient safety margin is provided, an A:W ratio of 60:1 was selected for the preliminary design.

## 3.5.3 Removal Efficiency

The data shown in Table 4 reflect the effectiveness of air-stripping for the removal of all the VOCs detected at the site. Removal efficiency for the 10-feet of packing media used in testing varied as follows:



Generally, 1,2-DCE was more difficult to remove than any of the other VOCs. During the test, all but vinyl chloride were consistently removed to effluent concentrations less than the proposed EPA discharge limits.

The relationship between packing height and percent removal for each VOC is illustrated in Figure 4. This relationship was developed for a 0285-23-1125<br>0285-23-1125 -12-

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liquid loading rate of 30 gpm/sf and an A:W ratio of 60:1. Using vinyl chloride and 1,2-DCE as the critical compounds for design, a column height of 22 feet was selected. Under these conditions, the following removals could be expected:



The expected effluent concentrations are less than or equal to the EPA recommended effluent criteria.

## 3.5.4 Column Design Parameters and Criteria

As determined from the evaluation presented above, the following design criteria are recommended:



#### 3.5.5 Scaling and Plugging of Column Internals

The potential for fouling, plugging or scaling of the air-stripping system was evaluated. The primary concern is associated with the presence of elevated iron and manganese concentrations in the ground water and the oxidation of iron and subsequent precipitation of ferric hydroxide on the air-stripping column internal. Ground water in the Northeastern United States is generally low in carbonate, and scaling due to calcium carbonate deposition has not been a major operating problem experienced by other Malcolm Pirnie applications.

The total iron concentration in the ground water at the site during the field investigation ranged from 0.06 to 80 mg/1, while the soluble



iron concentration ranged from 0.02 to 21 mg/1. The total iron concentration in the ground water used for treatability testing was approximately 4.3 mg/1 (see Section 5.3). Vendors of air-stripping equipment have indicated that, at iron concentrations between 2 and 12 mg/1, the air-stripper would require maintenance (such as an acid wash) every 2 to 4 months, while at concentrations less than 0.5 mg/1, no maintenance of packing materials would be expected (see Appendix B).

At present, the ground water collection system is expected to capture ground water from a large portion of the site. The wide range of iron concentrations detected in the ground water during the previous investigations suggests that the average air-stripper influent iron concentration will be between 2 and 12 mg/1. At the conclusion of the two weeks of field testing, the packing material which was removed from the pilot-scale air-stripping tower was stained brown, probably as a result of iron oxidation. No evidence of bacterial growth or mineral deposits was noted. Given the results of the field testing, the following design options and/or operation procedures should be considered:

- Weekly inspections of the internal packing material for the first six months of operation, followed by monthly inspections thereafter for the first year of operation. The frequency of inspections may be reduced after the first year of operation, if appropriate.
- Installation of an acid wash or acid bath (for example, 2% HCL) system to clean deposits before they affect operation and/or periodic removal and washing of the packing material.
- Monitoring of total iron and manganese concentrations before and immediately after air-stripping to determine rates of deposition.
- Installation of a batch chlorine addition system to control potential growth of iron bacteria in the air-stripping column.

It should be recognized that the maintenance of the system may require that the ground water extraction system be periodically shut down for periods of 24 to 72 hours.

While placing the chemical treatment of the ground water for metals removal before the air-stripper may reduce the air-stripper maintenance requirements, an additional step would be required to oxidize the iron before chemical precipitation. A chemical feed system to add an oxidant 0285-23-1125 -14-

such as peroxide or permanganate will be needed, which will offset the savings in maintenance of the air-stripper. Moreover, potential plugging of the air-stripper resulting from the deposition of other inorganic salts may still necessitate periodic cleaning of the column internals.

## 3.5.6 Air Quality

The concentration of VOCs in the air exiting the column depends on the mass of the compound removed from the water and volume of air used during the air-stripping process. Based on the design conditions for influent and effluent VOC concentrations, the water flow rate and the volume of air used, a mass balance was determined for the process. The results are presented in Table 5.

Although an air discharge permit will not be required for the treatment system, the "Interim Operating Guidance for Air Toxic Substances: New and Modified Sources" issued by the Pennsylvania Department of Environmental Resources (PADER) in September 1985 and the Permissible Exposure Levels (PELs) developed by OSHA were used as a basis for determining if VOC concentrations in effluent air would exceed acceptable, health-based criteria. The effluent air concentration for each VOC was calculated assuming 100% of the design ground water influent concentration is transferred to the air. As can be seen from Table 5, the effluent air concentration for each VOC is substantially less than either the occupational exposure limit or the ambient concentration established by PADER. Based on this analysis, the use of air emission controls will not be required.

#### 4.0 ORGANICS REMOVAL USING GRANULAR ACTIVATED CARBON

#### 4.1 PURPOSE

In order to determine design criteria for a granular activated carbon (GAC) adsorption system for the further removal of organic compounds from the ground water following treatment by air-stripping, laboratory bench-scale testing was performed. The testing occurred in two steps. Adsorption isotherms were first developed to evaluate two types of GAC.

Based on this evaluation, one type of GAC was selected for use in a bench-scale GAC mini-column adsorption test. Total organic carbon (TOC) and biochemical oxygen demand (BOD) were used as indicators for the adsorption of organics by GAC.

The intent of developing the adsorption isotherms was to evaluate the adsorptive capacity of two different types of carbon and to determine if GAC treatment should precede or follow VOC removal by air-stripping. The intent of the GAC mini-column test was to determine design criteria for further removal of the critical organic compounds from the ground water following treatment by air-stripping.

## 4.2 ADSORPTION ISOTHERMS

## 4.2.1 Method

GAC samples from two vendors were selected for testing: Calgon F300 (8x30 mesh) and Darco HD-4000. As each carbon was to be tested both before and after VOC removal by air-stripping, influent (raw) and effluent (air-stripped) water samples were collected from the air-stripping tower 60 minutes after air-stripping Trial Run No. 3 had commenced (liquid loading rate of 19 gpm/sf at A:W ratio of 30:1). For each sample, a volume of 800 ml. was collected from the air-stripping column's sampling ports in a 1-liter graduated cylinder and transferred into 1-liter amber glass bottles sealed with air tight teflon-lined caps. After all the samples were collected, a pre-weighed quantity of GAC was added to each sample. Five GAC dosages were used for each test: 5, 10, 25, 50 and 100 grams. Table 6 contains a description of each sample tested.

After the carbon was added to each sample, the bottles were capped and swirled by hand. All samples were then placed on a shaker table for 20 hours to insure continuous contact with the carbon. In addition, each sample was swirled by hand hourly during the last 6 hours of the shaking. After a contact time of 20 hours, each sample was filtered through a Whatman GF/B glass fiber filter to remove carbon fines. The samples were subdivided for TOC and BOD analysis. TOC samples were preserved with sulfuric acid to a pH less than 2. BOD samples were placed on ice.

In addition to the 20 samples collected for the batch test, four samples (two each of influent and effluent) were collected as control samples with no treatment. One sample each of influent and effluent did not receive carbon treatment, to determine if shaking alone had any effect on the TOC and BOD concentrations. A second set of control samples did not receive carbon, nor were they shaken to determine the effect of both shaking and carbon addition.

#### 4.2.2 Results and Discussion

The BOD of each sample was less than 2 mg/1 (detection limit), suggesting that the organic carbon present in the samples was too low in concentration to exert a BOD or was not in a readily biodegradable form. The results of TOC analysis are presented in Table 6. These results were used to develop the adsorption isotherm illustrated in Figure 5. The TOC concentrations in the control samples did not seem to be affected by the air-stripping and sample handling processes. The two samples which received neither carbon or shaking had TOC concentrations of 12 and 13 mg/1 for the air-stripped and raw water samples, respectively. The TOC concentration in both control samples which were shaken without added carbon was 11 mg/1; shaking alone produced no appreciable decrease in the TOC concentrations. Therefore, any changes in TOC concentrations in the samples used in the isotherm test were attributed to adsorption of TOC by the activated carbon. The control samples were used as representative of the starting conditions to determine the adsorptive capacity of the activated carbon.

The relatively low total concentration of volatile organic compounds in the ground water, when compared to the elevated TOC concentration, indicates that the organic carbon present in the samples is not due to VOCs. The total VOC concentrations in the raw and air-stripped ground water were approximately 0.92 mg/1 and 0.1 mg/1, respectively. The TOC concentration was approximately 12 mg/1 in the raw ground water. Since neither VOCs or semi-volatile organic compounds were present in sufficient concentration to account for the measured TOC concentrations, it is probable that the total organic carbon in the ground water is primarily from naturally-occurring fulvic and humic acids.

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The results summarized in Table 6 indicate that, at a carbon dosage of 6.25 g/1, Calgon F300 offered better TOC adsorption (1.55 mg/gm) that the Darco HD-4000 (1.08 mg/gm). In addition, Calgon F300 carbon removed the TOC to below the detection limit (1 mg/1) at carbon doses greater than 6.25 g/1. Although there was little apparent difference in the final TOC concentrations between the raw and air-stripped water, the second phase of GAC testing was performed using air-stripped water. As it offered slightly better adsorptive capacity, the Calgon 300 carbon was selected for use in the mini-column system.

#### 4.3 BENCH SCALE MINI-COLUMN TEST

## 4.3.1 Description

A bench scale mini-column system was set up to develop breakthrough curves for TOC, VOCs, semi-volatiles and BOD. The mini-column system, illustrated in Figure 6, consists of a precision flow metering pump, stainless steel tubing, dampening cylinder and pressure gauge. The water sample reservoir was a sealed 2.5-gallon glass container; Teflon tubing was used as a suction line from the reservoir. The mini-column was of 1/4-inch I.D. stainless steel tubing; the carbon was held in place with glass wool.

## 4.3.2 Operation

An air-stripped water sample was collected from the air-stripping tower while operating at a liquid loading rate of 20 gpm/sf and A:W ratio of 20:1 after completion of the air stripper Trial Runs. The sample was stored on ice overnight and during the testing.

Calgon F300 was selected for testing based on the results of the isotherms for TOC removal. The carbon was pulverized and sieved to a particle size range of 100 to 200 mesh. Based on the adsorption isotherms, it was initially determined that a carbon bed depth of 8-inches would possibly provide greater contact time and allow better breakthrough characteristics with respect to TOC and semi-volatiles. However, due to the characteristics of the ground water at the site and the size distribution of the pulverized GAC, high pressure drops developed at bed

depths greater than 1.5-inches. A bed depth of 1.5-inches with pressure drops of 60 to 120 psi was therefore used for the mini-column testing.

Approximately 1.5-inches of carbon was placed in the mini-column above a glass wool pack. The carbon was compacted in the column by tapping the column repeatedly on the counter top. The system was allowed to purge with sample prior to attaching the mini-column. The pump settings had been pre-adjusted to a flow of 15 ml/minute. Sampling of the mini-column effluent commenced immediately at the start of the test.

## 4.3.3 Sampling

The air-stripped water was run through the column containing 0.31 grams of carbon. A total of four samples of the mini-column effluent was collected for analysis of VOC, TOC, semi-volatiles and BOD. One sample of the air-stripped water was collected from the sample reservoir just prior to commencing the test. A summary of the sample intervals is presented in Table 7. Samples for TOC, semi-volatiles and BOD were split from a composite column effluent sample of approximately 1650 milliliters. Discrete VOC samples were collected in 40 ml vials. Samples were collected and preserved as described in Table 8.

## 4.3.4 Results and Discussion

The results of the GAC mini-column test are summarized in Table 9. The concentrations of VOCs and semi-volatiles in Table 9 are as reported by the laboratory for the water samples. The quantitation limits for organics in water are generally an order of magnitude lower than the reported instrument detection limits. Most laboratories therefore report the estimated concentrations of organics which are detected in the samples with a "J" qualifier if they are less than the detection limits.

Sample number GAC-0 represents the water quality of the air-stripped ground water used as influent to the carbon mini-column. At the operating conditions of the air-stripping tower at the time of sampling (liquid loading = 20 gpm/sf, A:W ratio = 20:1), the mini-column influent sample contained no critical organic compound of interest (viz. 1,1,1-trichloroethane, trichloroethene, 1,1-dichloroethene and vinyl chloride) at a concentration greater than the EPA's proposed effluent concentration (see



Table 4). Semi-volatiles compounds were present in the mini-column influent sample at less than the detection limit. Based upon the results of the ground water sampling performed in June 1988, the occurrence of semi-volatiles in the raw ground water is extremely variable and, therefore, not expected to be critical to the design process.

The ratios of the contaminant effluent concentrations to the influent concentration (Ce/Ci) are summarized in Table 9. Contaminants which were detected in the mini-column effluent but not in the influent are represented by asterisks (\*). Generally, these contaminants were present at less than the quantification limit and, therefore, are presented as estimated concentrations. The presence of compounds such as Di-n-butyl phthalate, Bis(2-ethyl hexyl) phthalate and Butylbenzyl phthalate in both the mini-column influent and effluent samples indicates that breakthrough may have occurred prior to or during the first sampling interval. Compounds such as TCE, vinyl chloride, 2-methyl-napthalene and napthalene which were present in the influent but were not detected in one or more effluent samples indicates that the carbon adsorbed these particular compounds. However, because these contaminants were present in both the mini-column effluent and influent at concentrations near or below the detection limit, the quantity of organics removed by GAC adsorption was difficult to determine.

Only 1,2-DCE and TOC were consistently present in the mini-column influent and effluent at concentrations sufficient for a quantitative evaluation of the carbon adsorption system. The Ce/Ci ratios for 1,2-DCE indicate that breakthrough was first detected in sample GAC-2 at a concentration of 9 ug/1 after 1755 ml of water had passed through the column. The effluent 1,2-DCE concentration steadily increased to 66 ug/1 (Ce/Ci=0.70) in the final VOC sample (GAC-4) collected after 5206 ml had passed through the column. A breakthrough curve showing the Ce/Ci ratios for 1,2-DCE plotted against the sample volume passed through the column is illustrated in Figure 7.

The adsorptive capacity of the carbon for 1,2-DCE was determined from the area under the breakthrough curve. At an effluent 1,2-DCE concentration of 70 ug/1 (design criteria), representing a 30 percent removal, the adsorptive capacity of the carbon is 1.2 mg/gram carbon. To L

achieve an effluent concentration of 5 ug/1, the adsorptive capacity of the carbon would be reduced to 0.3 mg/gram carbon.

The TOC concentrations in the mini-column effluent were extremely variable and did not display a steady increase in effluent concentration with time. The first composite effluent sample, GAC-1, had a TOC concentration of 4.7 mg/1, indicating that breakthrough had occurred. However, the TOC concentration in samples GAC-2 and GAC-4 substantially exceeded the influent TOC concentration of 12 mg/1. These elevated TOC effluent concentrations may be due to GAC fines passing through the glass wool filter pack in the mini-column.

The Ce/Ci ratios for TOC are also plotted in Figure 7. As the TOC samples were each split from composite sample intervals of approximately 1650 ml, the Ce/Ci ratio was plotted at the midpoint of each sample interval. The adsorptive capacity was, therefore, based on breakthrough occurring after 940 ml of water had passed through the mini-column. The adsorptive capacity of the carbon for TOC removal was determined using the effluent sample GAC-1 as representing the breakthrough point. At the TOC effluent concentration of 4.7 mg/1, representing a 61% removal, the adsorptive capacity of the activated carbon is 33 mg/gram of carbon. This value, however, does not correspond to the adsorptive capacity of 1.5 mg/gram determined from the batch isotherm test.

The air-stripped water sample used for the mini-column testing contained relatively low concentrations of volatile and semi-volatile (A/B/N) organic compounds; the total VOC and semi-volatile concentration was approximately 0.1 ug/1. The results of the air-stripping test indicate that the total VOC and A/B/N compound concentration in effluent samples will not exceed 0.4 mg/1. As the TOC concentration in both the air-stripped and raw ground water samples is approximately 12 mg/1, it is apparent that the organic carbon may be representative of naturallyoccurring fulvic and humic acids.

The results of the GAC mini-column test indicate that:

- total organic carbon (TOC) is probably present in the ground water as naturally occurring organic acids and should not be used as a design criteria.
- the adsorptive capacity of Calgon F300 for removing 1,2-DCE is 0.3 mg/gram and 1.2 mg/gram for mini-column effluent concentrations  $\frac{37}{100}$  and 70 ug/1, respectively.<br>0285-23-1125 -21-



- the critical organic compounds of interest (1,1,1-TCA, 1,1-DCE, TCE and Vinyl Chloride) were not present in the mini-column influent, as they were effectively removed by air-stripping.
- semi-volatile organic compounds were generally present at or below detectable concentrations in the GAC column influent.
- the use of carbon adsorption for the removal of organic compounds from air-stripped effluent is not warranted for this site.
- 5.0 BENCH SCALE TESTING FOR INORGANICS REMOVAL
- 5.1 INTRODUCTION

Bench scale testing was performed to evaluate chemical precipitation methods to remove inorganic contaminants (viz. metals) from ground water prior to and following air-stripping. The purpose of the tests was to:

- determine appropriate precipitants and dosages, and
- determine settling times, sludge production rates, and simulated effluent qualities.

Specific tests performed as part of the bench scale testing included:

- titration curves,
- jar testing,
- long-tube testing, and
- sludge thickening.

## 5.2 TITRATION CURVE

Titration curves were developed using caustic (NaOH) and lime  $(Ca(OH),)$  on both raw ground water and ground water treated by airstripping. The purpose of the titration curves was to establish dosages of precipitants needed to adjust the pH of the ground water in order to promote removal of metals via precipitation. Both sodium hydroxide and calcium hydroxide were used for the titration curve development and were evaluated during the jar testing.

The titration curves were developed using a paddle stirrer, pH meter, and stock solutions of precipitants. The samples used for developing the

titration curves were collected during Trial Run 4 on the air-stripping column. Approximately 1500 gallons of the ground water tested during this run had been pumped into the storage tank 12 to 15 hours prior to commencing the test. In addition, ground water was also pumped into the tank during the air-stripping test. The air-stripping test was performed at a liquid loading rate of 20 gpm/sf and 40:1 A:W ratio. The procedures followed for developing each titration curve were as follows:

- 1. Calibrated pH meter using two point calibration technique.
- 2. Measured 500 ml of sample into beaker, placed beaker on paddle stirrer.
- 3. Secured pH probe in sample and recorded initial pH.
- 4. Added stock solution of titrant (0.1N NaOH or 0.27N lime) to the sample in 1-2 ml increments, allowing pH to stabilize, and recorded total stock solution added and pH of sample. Note that stock solutions were made from NaOH-lN and 10% reagent grade lime.

The titration results are summarized in Table 10; Figures 8 and 9 illustrate the titration curves developed from the data in Table 10. As shown in Table 10, the raw ground water required the addition of 60 to 100 percent more base than the air-stripped water to achieve a pH of 9 s.u. To raise the sample pH to 9.0 s.u. using NaOH, approximately 1.2 meq/1 was used for the air-stripped sample, while 1.9 meq/1 was needed for the raw ground water sample. Similarly, using lime to achieve a pH of 9.0 s.u. required 1.5 meq/1 for the air-stripped water, while more than twice the amount (3.1 meq/1) of lime was required for the raw water sample. These differences may be due in part to the removal of carbonate as CO<sub>2</sub> during air-stripping.

As shown in Figures 8 and 9, the incremental addition of lime and caustic to both the air-stripped and raw ground water samples resulted in a rapid increase in pH to approximately 9 s.u., then a slow increase to

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pH of 10.5 s.u. The amount of base required for this incremental change in pH from 9.0 to 10.5 s.u. is shown below:



These results indicate that significantly less base is required to achieve a pH of 9.0 than 10.5 s.u. The air-stripped ground water also requires less base than the raw water required to achieve the same pH.

## 5.3 JAR TESTS

## 5.3.1 Description

Bench scale testing for inorganics removal was performed with the aid of a 4-paddle stirrer, 500-ml beakers, and chemical precipitant. These jar tests were designed to determine the optimum chemical precipitant for both raw and air-stripped ground water. Initial performance evaluations were based on turbidity measurements of the samples prior to and after chemical precipitation. The initial evaluations were supported by collecting one supernatant sample from each jar test for analysis of total suspended solids (TSS) and total and soluble iron, chromium, lead, manganese, copper and zinc. Control samples of the untreated raw and airstripped water were submitted for analysis of TSS, and total and dissolved metals.

The jar tests were performed on both raw ground water (influent) and ground water treated by air-stripping (effluent). Four treatment scenarios were evaluated for both water types, including:

- pH adjustment using only sodium hydroxide;
- pH adjustment using only lime;
- adding sodium sulfide at  $75%$  of the total iron concentration prior to pH adjustment with lime; and ^^  $0285 - 23 - 1125$  -24-





- adding sodium sulfide at 125% of the total iron concentration prior to pH adjustment with lime.

Iron is present in the ground water as the ferrous ion, which is easily oxidizable to the ferric ion in the air-stripper. Ferrous sulfide is more insoluble than ferrous hydroxide. However, ferric hydroxide has the least solubility compared to the others. The testing for metals removal therefore included both hydroxide and sulfide precipitation. In the case of testing for sulfide precipitation, sodium sulfide was added prior to pH adjustment to allow for the preferential formation of insoluble metal sulfides. Sodium sulfide also raises the pH, thereby requiring less lime or caustic to subsequently adjust the pH.

#### 5.3.2 Procedures

Samples for testing were collected from the air-stripping tower. The air-stripping tower was operated at a liquid loading rate of 17 gpm/sf and A:W ratio of 60:1. Ground water was pumped from both wells MW-9 and MW-10 into a 35-gallon plastic equalization basin and subsequently to the top of the tower. After the system had equilibrated (approximately 20 minutes), samples of the stripping tower influent and effluent were collected in plastic jugs.

For each jar test, the samples were divided into four-500 ml aliquots and placed in the four beakers on the paddle stirrer. The initial sample pH and turbidity was recorded. The pH was then adjusted to pH 7, 8, 9 and 10 s.u. by adding either sulfuric acid, lime or sodium hydroxide. As the initial pH was generally greater than 7 s.u., sulfuric acid at a stock solution concentration of 0.4% (0.008N) was used to lower the pH to 7.0. The pH, turbidity and volume of precipitant added were then recorded after the sample pH had stabilized. The four samples were rapidly-mixed for 60 seconds, flocculated (slow mix) at 10 rpm for 15 minutes and allowed to settle undisturbed for 60 minutes. To aid in coagulation and settling, an anionic polymer was added to each sample at a concentration of 0.5 ppm while rapid mixing.

After settling, the supernatant turbidity was measured by withdrawing a sample with a syringe. Based upon a visual assessment of the solids removal and lowest supernatant turbidity, one supernatant sample from each

set was withdrawn for analysis of TSS and total and soluble metals. All samples were preserved in accordance with Table 8. Samples for dissolved metals were filtered by positive pressure through a 0.45-micron filter.

The turbidity measurements taken during the first four jar tests (evaluating the addition of lime vs. sodium hydroxide) indicated that the lime provided slightly better solids removal than sodium hydroxide. Therefore, the remaining four tests were performed to evaluate the effectiveness of the addition of two different concentrations of sodium sulfide in conjunction with lime. Sodium sulfide was added prior to pH adjustment at 75% and 125% of the total iron concentration expected in the ground water. The total iron concentration in ground water sampled from MW-9 in June 1988 was 16 mg/1, while MW-10 contained 9.3 mg/1 in a sample collected during the previous RI. Therefore, an anticipated average total iron concentration of 12 mg/1 was used to determine the amount of sulfide which was added.

## 5.3.3 Results

The testing conditions and initial performance evaluations are summarized in Table 11. Supernatant samples were collected for analysis based upon three criteria: pH, turbidity (% removal) and settling characteristics. Generally, the pH of a direct discharge is limited to a maximum of 9.0 s.u. Therefore, if the other criteria were acceptable, supernatant samples at pH 9 s.u. are preferred over a higher pH. The supernatant with the maximum percent removal based on the turbidity measurements was generally selected for analysis. A medium to large floe is preferred over fine flocs, which take longer to settle.

The raw ground water initially had a low turbidity (average 4.7 NTU) relative to the air-stripped water (average 20 NTU). The change in turbidity of the raw water during air-stripping can be attributed to the oxidation of iron from the soluble +2 state (ferrous) to the relatively insoluble +3 state (ferric).

It was observed that, for raw and air-stripped water samples which were allowed to stand in one-liter beakers exposed to the atmosphere, the raw water turbidity increased from 1.8 to 15 NTU in a five-hour time period, while the air-stripped water turbidity remained unchanged at 15

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NTU over the same time period. A fine, reddish brown suspended solid was observed in both samples after the five hours had elapsed.

Sodium Hydroxide - Tests 1 and 2 were performed to evaluate the effect of pH adjustment using only sodium hydroxide. In both cases, a pH of 9 s.u. provided the best turbidity removal, making it suitable for direct discharge from a treatment system. The supernatant turbidity for the raw water sample (4.80 NTU) was slightly better than the air-stripped water sample (6.30 NTU).

Lime - Tests 3 and 4 were performed to evaluate metals removal by pH adjustment with calcium hydroxide (lime) only. The added lime significantly increased the initial turbidity of the samples. This is probably due to insufficient dissolution of lime or precipitation of calcium carbonate. For the raw ground water, supernatant turbidities at pH 9 and 10 s.u. were nearly equal (1.7. and 1.4 NTU, respectively). Similarly, supernatant turbidities for the air-stripped water sample were 3.6 and 2.8 NTU at values of pH 9 and 10 s.u., respectively. For both tests, a supernatant sample at pH 9 s.u. was submitted for TSS and metals analyses.

Sodium Sulfide - The results of tests 1-4 were evaluated before proceeding with tests 5-8. While the addition of lime increased the initial sample turbidity during pH adjustment, the settling characteristics and supernatant turbidity were slightly better with lime than with sodium hydroxide. In addition, the cost of lime is generally less than the cost of sodium hydroxide, making lime an economical choice in situations where the results of the jar tests are relatively equal. Even though more sludge will be generated using lime than caustic, this sludge may have better TCLP characteristics, rendering it non-hazardous. Therefore, lime was used for pH adjustment for tests 5-8.

Tests 5 through 8 were performed to evaluate the effectiveness of adding a sulfide salt to aid in precipitation. A characteristic "rotten egg" odor and black precipitate was noted after adding sodium monosulfide to the raw ground water sample for tests 5 and 7. This is probably a



result of the formation of  $H_2S$  and the precipitation of iron in the raw water as ferrous sulfide. During air-stripping, or exposure to the atmosphere, the iron is oxidized to the +3 state, forming the more stable ferric oxide precipitate. Under these conditions, the iron was unavailable to react with the sulfide, as in the air-stripped water samples used in tests 6 and 8.

Supernatant turbidity measurements summarized in Table 11 indicate that the addition of sodium sulfide at a concentration of 9 mg/1 (75% of iron concentration) yielded slightly improved removals when compared to the addition of 15 mg/1 (125%). For example, for the air-stripped water samples (JT-6, JT-8), the final supernatant turbidity was 2.80 and 4.35 NTU with the addition of 9 and 15 mg/1 sodium sulfide, respectively. For each test, the sample at pH of 9 s.u. appeared to provide the best removal and was, therefore, submitted for analysis of TSS and total and dissolved metals.

The final pH of the supernatant samples submitted for analysis was taken to determine if any changes had occurred during the testing. These are summarized in Table 11. The pH of samples JT-1 through JT-4 were measured 12 hours after the sample was collected, while JT-5 through JT-8 were collected approximately one hour after the sample was collected. The results indicate that, while the pH was initially adjusted to 9.0 s.u., the samples appeared to stabilize at approximately 8.5 s.u., regardless of which precipitant was added.

Iron Removal - Table 12 summarizes the analytical results for selected supernatant samples and the two (raw and air-stripped water) control samples. The effect of air-stripping on the oxidation state of iron is demonstrated by the analytical results for the control samples. Of the total iron concentration of 4.3 mg/1 in the raw water (JT-RAW), 3.2 mg/1 is soluble because of the higher solubility of the ferrous form. The soluble iron concentration was 0.05 mg/1 in the air-stripped water (JT-TRT), confirming that the iron was oxidized to the insoluble ferric state and precipitated as ferric hydroxide during air-stripping. This reduction in soluble iron by air-stripping alone was sufficient to achieve the EPA-proposed discharge limit of 0.3 mg/1 for soluble iron. However,

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air-stripping alone has no influence on the total iron concentration. Each treatment type successfully reduced the total iron concentration to less than the EPA-proposed discharge limit of 1.5 mg/1. Supernatant total iron concentrations ranged from 0.09 mg/1 (98% removal) in the raw water sample treated with only lime (JT-3) to 0.33 mg/1 (92% removal) in an airstripped water sample treated with NaOH only (JT-2). The lower total and soluble iron concentrations in the treated air-stripper influent samples is due to the oxidation of iron and subsequent precipitation of ferric hydroxide during the jar test. Assuming a design total iron concentration of 12 mg/1, and a discharge limit of 1.5 mg/1, each treatment method tested is capable of meeting a design removal efficiency of 88%.

Manganese Removal - Air-stripping alone had no effect on the soluble or total manganese concentration. Although the total manganese concentrations were reported by the lab (Table 12) as slightly less than the soluble manganese concentrations, there is no statistically significant difference between the values. Therefore, it was assumed that manganese present in each sample is in the insoluble form.

The removal rates for total manganese ranged from 64% using only NaOH in the air-stripped water to 99% using only lime in the raw water. The EPA has proposed a discharge limit of 1 mg/1 for the treatment system. As the total manganese concentration in the raw ground water used for the jar tests was 0.45 mg/1, this discharge limit is not a limiting design factor for this treatment system. The maximum manganese concentration detected in the ground water during sampling in June 1988, was 2.8 mg/1; assuming this as the design influent concentration yields a required removal efficiency of 64% to meet the discharge limit of 1 mg/1. As lime provided better removal efficiency for both the raw and air-stripped water, the use of lime is recommended to ensure that the discharge limit for manganese is met.

Chromium and lead were not detected in the influent ground water samples, confirming the results of ground water sampling performed during the Remedial Investigation in 1984 and in June 1988. Each type of treatment successfully removed TSS to less than 2 mg/1 from an initial TSS of 11 mg/1.

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### 5.4 LONG TUBE TESTING

5.4.1 Description

The purpose of the long tube tests was to determine settling rates and clarifier surface overflow rates. An evaluation of the settling characteristics and supernatant turbidity during jar testing indicated that optimum settling conditions for raw ground water occurred at a pH of 9.0 s.u. after the addition of lime and sodium sulfide, while for the air stripper effluent, adjustment to a pH of 9.0 s.u. using lime provided sufficient metals removal. Therefore, these conditions were replicated for the long tube test.

The long-tube apparatus shown in Figure 10 consisted of a 4-inch diameter plastic tube, 6'-9" tall, with six sampling ports at 1-foot intervals along the side. A drain in the base of the tube allowed the sample to be drained at the completion of the test. Samples were collected from each port through a flexible rubber hose equipped with a clamp.

### 5.4.2 Procedures

Five gallons each of raw and air-stripped ground water was collected while the air-stripping column was operated at a liquid loading rate of 17 gpm/sf and a 60:1 A:W ratio. The system was operated for approximately 20 minutes before collecting the samples. The raw water was first treated with 28.4 ml of 1% sodium sulfide corresponding to a dosage of 15 mg/1. Approximately 11 ml of 10% Ca(OH), solution was then added to raise the pH to 9.0 s.u. An anionic polymer (Betz 1100) was added (19 ml of 0.05% solution) at a dosage of 0.5 ppm. The solution was then rapidly stirred with a wooden stirrer for approximately one minute. Using a large funnel, the sample was poured into the settling tube, which was held at an angle to minimize air entrapment. A stopwatch was started as soon as the tube was returned to a vertical position.

Samples for turbidity measurements were collected in 4-ounce plastic cups at pre-determined time intervals. Each sample was completely mixed with the aid of a syringe prior to the turbidity measurement.

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The air-stripped water sample was treated by adding approximately 7.5 ml of 10% Ca(OH), to raise the pH to 9.0 s.u. The anionic polymer was added to a concentration of 0.5 ppm. The sample was then stirred and tested as described above. The results of the long tube tests are summarized in Table 13.

### 5.4.3 Long Tube Test Results and Discussion

### 5.4.3.1 Raw Water

The turbidity measurements from each long tube test are presented in Table 13. The raw ground water (air stripper influent) sample had an initial turbidity of 1.3 NTU; after treatment with lime and sodium sulfide, the turbidity averaged 90 NTU across the full depth of the column. The increase in turbidity was due to the precipitation of ferrous sulfide, visually observed as a black floe.

The turbidity in the top two sampling ports varied between 20 and 35 NTU during the second hour of the test. During the jar tests, the supernatant turbidity for similar chemical treatment of the raw ground water ranged from 2.3 to 3.3 NTU after settling for 60 minutes. The elevated turbidity in the long tube after 60 minutes of settling is probably a result of the floe being sheared while transferring the sample from the mixing container to the long tube; the fine floe resulting from the shear would have lower settling velocities than expected, based on the jar tests. Observations during the jar tests indicated that the floe settled rapidly (generally within 5 minutes) to the bottom of the beaker.

Assuming that the turbidity remaining in the sample after 60 minutes of settling is largely due to fine floe, the changes in turbidity during the first hour of the test is due to the rapid settling of larger, easily settleable solids. Under worst case conditions, the unhindered settling velocity of a particle at the surface of the water would be 0.1 ft/min (6 feet/60 minutes), resulting in a clarifier surface loading rate of 1077 gpd/sf.



### 5.4.3.2 Air-stripped Water

The initial turbidity of the air-stripped water was 26 NTU prior to chemical addition and greater than 100 NTU after treatment with lime to adjust the pH to 9 s.u. The turbidity in the top sampling port decreased to 39.5 NTU within 10 minutes and changed little over the next 50 minutes; the turbidity at the remainder of the sampling ports remained greater than 100 during the first 10 minutes of the test. The turbidity generally decreased across the entire column after the first 10 minutes and reached a minimum after 60 minutes of settling.

The observed supernatant turbidity during the jar test was 3.6 NTU after 60 minutes of settling. In comparison, the turbidity at the top sampling port of the long tube was 38 NTU. The elevated turbidity is again due to floe shear which occurred during sample transfer to the long tube. The large floe observed during the jar test settled rapidly (within 5 minutes).

As the turbidity was reduced to a minimum after 60 minutes of settling, it can be assumed that the majority of particles had settled by this time. The estimated unhindered settling velocity would be 0.1 ft/min (6 ft/60 min) under these conditions. In actuality, the settling velocity may be greater, which would result in a greater surface loading rate.

### 5.5 SLUDGE DISPOSAL

### 5.5.1 Description

In order to establish the design criteria for dewatering and disposal of the sludge generated as a result of the inorganic removal by precipitation, it was necessary to perform batch-scale testing to generate a sufficient quantity of sludge to evaluate:

- sludge thickening characteristics
- dewatering characteristics
- chemical characteristics of sludge filter cake leachate by TCLP.

Initial assumptions while developing the scope of work for this phase indicated that approximately 500 gallons of ground water was to be treated in 55-gallon barrels on-site. However, a sample of treated water

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collected during the long tube test contained approximately 0.1% solids by volume. Given that a total of 10 gallons of sludge was required for the sludge dewatering tests, it was necessary to treat a minimum of 10,000 gallons of ground water. Therefore, the temporary storage tank was utilized to generate the required volume of sludge. Because the storage tank held only 6500 gallons, it was necessary to perform two batch tests on successive days.

### 5.5,2 Batch Scale Test Procedures

A preliminary evaluation of the jar test results indicated that the optimum chemical treatment was achieved following volatile organics removal by air-stripping. To supply water for this batch test, the airstripper was operated at a liquid loading of 19 gpm/sf and A:W ratio of 50:1. Ground water was pumped from wells MW-9 and MW-10, through an equalization basin and into the top of the tower. The air-stripped effluent was discharged by gravity to a temporary holding basin, then pumped into the 6500-gallon stainless steel tank for settling. USP-grade calcium hydroxide (minimum  $95%$  Ca(OH)<sub>2</sub>) was added to the air-stripped ground water at the rate of one pound per thousand gallons to adjust the pH of the water to 9.0 s.u. The ground water was recirculated in the tank to aid in mixing and flocculating. An anionic polymer was added to a recirculating pump and the treated water was recirculated for approximately one hour after polymer addition to ensure adequate mixing and flocculation.

Prior to beginning either batch test, the tank was flushed clean using a spray wash and ground water pumped from MW-9. A volume of 5615 gallons of air-stripped ground water was treated during BT-1, while 5343 gallons were treated during BT-2.

During pH adjustment, pH measurements of the tank water were taken to monitor the lime addition process. A total of 2.26 kg (5 pounds) of USP-grade lime was added during BT-1, while 2.72 kg (6 pounds) of lime was added during BT-2. While a pH of 9.0 s.u. or greater was observed during the pH adjustment, the pH equilibrated at 8.4 s.u. prior to polymer addition. This seems to correlate with the pH equilibrium observed in supernatant samples during the jar testing.



The solids were allowed to settle undisturbed in the storage tank prior to decanting the supernatant. For batch test 1 (BT-1), the settling time was approximately 64 hours. The settling time for batch test 2 (BT-2) was approximately 12 hours. The supernatant was pumped from the tank and discharged to the on-site pond. After the supernatant was decanted, a spray wash was used to flush the sludge from the bottom of the tank into 35-gallon plastic containers, where the "flush water" was decanted.

### 5.5.3 Gravity Thickening Test

A sample of sludge and a sample of supernatant from batch BT-1 were retained for a gravity thickening test. Three one-liter graduated cylinders were used to determine the thickening characteristics at dilutions 25%, 50% and 75% by volume using sludge and supernatant. The desired volume of well-mixed undiluted sludge was first measured into a graduated cylinder, then supernatant was added until a volume of 1000 ml was obtained. After the sludge was thoroughly mixed, it was allowed to settle and the interface between the sludge and the clear supernatant was recorded at predetermined time intervals. The results of the thickening test are summarized in Table 14. Figure 11 illustrates the change in interface height with time for each mixture.

Initially, in all three mixtures, the solids concentration appeared uniform throughout the column. The interface was apparent within one minute in the 50% and 75% mixtures. The interface was not easily distinguishable in the 25% mixture in the first 15 minutes due to the relatively dilute nature of the mix.

The initial TSS of the sludge was 178,000 mg/1, or 17.8% solids. Typically, sludge concentrations from clarifiers using lime precipitation range from 0.5 to 7 percent solids. A mass balance indicates that the removal of suspended solids initially present in the raw ground water contributed approximately 10% of the sludge produced; the remainder of the sludge consisted primarily of calcium carbonate, ferric hydroxide and, to a lesser extent, manganese hydroxide resulting from the addition of lime. The volume of the sludge was approximately 0.1% of the volume of treated water.

### MALCOLM PIRNIE

Based on Figure 11, the hindered particle settling velocity ranged from 0.01 ft/min. in the 75% sludge mixture (13% solids by volume) to 0.06 ft/min. in the 25% sludge mixture (5% solids by volume) during the first 5 minutes of the thickening test. After 15 minutes of thickening, the settling velocity was 0.01 ft/min. in each of the three mixtures. In spite of the elevated solids concentration, these velocities are generally greater than those observed for conventional systems. In addition, thickened sludge from conventional thickeners is typically less than 17 percent solids.

Given that the sludge volume is relatively low (0.1%) and the solids concentration relatively high (17.8%) compared to typical values for sludge from clarifiers, it is expected that a sufficient amount of settling and thickening can occur in a clarifier, and that a thickener is not required. At a flow of 100,000 gpd through the proposed treatment system, a sludge volume of 100 gpd would be expected. This volume can be easily handled by periodically pumping the sludge from the bottom of the clarifier; at this flow rate, a continuous underflow would not be necessary.

### 5.5.4 Sludge Dewatering Tests

The purposes of the sludge dewatering tests were to:

- evaluate two types of filter press dewatering methods; and
- determine disposal methods for dewatered sludge.

Two five-gallon samples of thickened sludge were collected for dewatering by two different methods. One sample was sent to a plate and frame filter press manufacturer (Duriron Co., Inc.), while the second was sent to a belt filter press manufacturer (EIMCO Process Equipment Company).

The initial solids content of the sludge sample used for dewatering by belt filter press was 17.5%. The belt press simulated was a gravity drain platform with a backup compression belt. An anionic polymer (Percol 727) was added at a rate of 3 mg/1 prior to filtration using EIMCO media type DA 6093. This media is rated at 360 cfm/ft (or 16% open pores). At a hydraulic capacity of 116 gpm/meter width of filter belt,

 $0285 - 23 - 1125$  -35-

### MALCOLM PIRNIE

the dewatered cake averaged 62% by weight solids.

A sludge cake dewatered by means of an EIMCO Shriver pressure filter contained  $67\%$  solids by weight, at a cake density of 71 lbs/ft<sup>3</sup> which is a slightly better performance than the belt filter press. The sludge pumping rate was 0.11 gpm/ft at a pressure of 80 psig.

A pressure filter test by Duriron on a sludge sample containing 27% solids produced a dewatered sludge cake of approximately 80% solids and density of  $110$  lbs/ft<sup>3</sup> at a pressure of  $100$  psi and loading of approximately 0.05 gpm/ft .

After the sludge was dewatered, each sludge cake was sent to Recra Environmental for analysis of TCLP contaminants listed in Federal Register, June 13, 1986, Part 261, Proposed Rule. Rather than extensively disturb the samples and risk the additional loss of VOCs just to place the samples in 40 ml-vials, the dewatered sludge cakes were shipped as they were received from the vendors (in airtight plastic bags or glass containers) to the lab. The lab subdivided the cakes for the required analysis. No refrigeration was used during sample shipment.

The TCLP analysis detected the presence of toluene, barium, cadmium, lead, silver and chromium in the extract of the two sludge cakes. The remainder of the parameters were not detected. The contaminants which were detected were present at concentrations less than the EPA maximum concentration limit used to characterize hazardous waste. The results summarized below indicate that the dewatered sludge cake could be disposed of as a non-hazardous waste, as the characteristics of the sludge do not exceed EPA's toxicity criteria.



# MAICOLM PIRNIE

### 5.6 DESIGN PARAMETERS

The preliminary clarifier design parameters based upon the results of the bench scale testing are as follows:



Typically, solids flux for clarifiers range between 20 and 30  $1b/day/ft^2$ . The relatively low solids loading makes the use of an inclined plate clarifier a desirable alternative for this site.

As previously stated, the elevated solids concentration of the sludge obtained by lime precipitation (17%) and the relatively low volume of sludge produced (0.1% by volume) in combination with an expected water flow rate of between 0.08 and 0.15 MGD makes the use of a sludge thickener impractical. Daily pumping of sludge from the bottom of a clarifier to a sludge holding tank should allow sufficient thickening to occur while eliminating the capital, operating and maintenance costs associated with a gravity thickener.

If on-site sludge dewatering, a plate and frame filter press offers the flexibility of being operated in a batch mode. This flexibility is desirable, given the relatively small quantity of sludge which will be produced daily. The desired design parameters for a filter press are listed below:



### 6.0 GROUND WATER TREATMENT SYSTEM

A computer evaluation of the ground water extraction system predicted an average ground water flow of 80,000 gpd from the proposed ground water extraction system. The treatment system is sized for a flow of 150,000 gpd to account for:

- inherent variability in the computer flow model (viz. variability in estimates of hydraulic conductivity, porosity, recharge and other hydraulic components of the model) which may underestimate the actual flow;  $\frac{1000}{37}$ <br>0285-23-1125 -37-



- anticipated high flow rates during start-up of the extraction system (when ground water drains from storage);
- elevated water table conditions during periods of high recharge rates (viz. snowmelt) which requires greater pumping rates to maintain drawdown conditions; and
- a safety factor of 2 for system design.

The treatment system will be designed to accept a wide range of flows up to 150,000 gpd. The extraction system is planned to allow one or more of the collection trenches to be shut down when ground water quality criteria are met. Therefore, the flows from the extraction system could range between 30,000 gpd and 150,000 gpd.

### 6.1 EVALUATION OF DISCHARGE ALTERNATIVES

As an alternative to providing full on-site treatment with discharge of treated ground water to Marshall's Run, the possibility of discharging either untreated or partially treated (air-stripped) ground water to the sewer was evaluated. This evaluation was undertaken to determine if a significant cost saving would be realized by minimizing the level of onsite treatment and utilizing the City of Erie wastewater treatment plant (WWTP) for treatment of the ground water. Since the City has combined sewers, flows as great as 100 MGD have been recorded at the WWTP during storm events. The WWTP presently has sufficient capacity to receive flows of up to 0.5 MGD from the Millcreek Site, except during storm flow.

The WWTP is designed for a daily TSS loading of 104,000 pounds per day (Ibs/day). The average daily loading is presently 75,000 Ibs/day. The daily BOD loading is approximately 90% of design capacity or 92,000 Ib/day; over 65% of this loading is from the paper manufacturing facility. Assuming that the ground water pumped from the Mi 11creek site has a TSS concentration of 15 mg/1, at a flow of 0.5 MGD, the additional TSS load to the WWTP would be 62 Ibs/day. The contribution of the ground water to the WWTP BOD loading is expected to be insignificant.

Three treatment options which were identified for evaluation of the effect of the level of treatment on sewer flows and WWTP operation were:

- no on-site treatment;



- on-site air-stripping; and
- on-site air-stripping and inorganics removal.

Based on discussions with representatives of the City and the EPA, the discharge of untreated ground water to the sewer was not feasible because:

- the potential for sewer overflows presents an unknown degree of risk to the public health; and
- the WWTP is a biological process and not intended for the removal of VOCs which may be present in the ground water.

Providing partial treatment (on-site air-stripping) will minimize the risk of exposure to VOCs by the public due to sewer overflows. Effluent from air-stripper would meet EPA's requirements with respect to volatile organics for direct discharge to Marshall's Run, and also meet the Erie WWTP permit requirements for discharge to the sewers. However, the airstripper effluent iron concentration would exceed EPA's direct discharge limits, but would be within the sewer discharge limits in a short time after start-up. Consequently, if ground water treatment only for VOCs is provided, the treated effluent can be discharged only to the sewer.

In addition to the concerns about public health, the City and Town of Millcreek were also concerned that the hydraulic capacity of the sewer in the vicinity of the site is limited. Hydraulic capacity improvements would probably be required should the alternative of discharging partially or fully treated ground water to the sewer be selected.

The current sewer use charge of approximately \$400 per million gallons would result in a cost of about \$22,000/year at the design flow rate of 150,000 gpd for discharge to the sewer. Additional capital costs would be required for a drainage pipe to the nearest sewer line, potential sewer capacity improvements, and hydraulic improvements at the WWTP. Due to these requirements and the City's concerns about the potential risk to the public that the discharge of partially treated ground water to the sewers presents, this option may not be feasible.

Providing full on-site treatment of the ground water for both VOCs and metals would result in an effluent water quality which would meet the EPA's limits for direct discharge to Marshall's Run (or to the sewers). Due to the additional capital costs and use charges associated with sewer

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## MAICOLM PIRNIE

and WWTP hydraulic capacity improvements, direct discharge to Marshall's Run is economically the better alternative under this treatment option.

### 6.2 TREATMENT SCHEME

The treatability testing results indicate that:

- air-stripping with counter current air flow in a packed column will provide sufficient removal of critical volatile organic compounds;
- organics removal with granular activated carbon is not required;
- inorganics removal by flocculation and precipitation will meet proposed effluent limits for iron and manganese; and
- the sludge does not exhibit leaching characteristics which would preclude disposal by landfilling.

A schematic of the proposed ground treatment system is shown in Figure 12. The design parameters are identified in Table 16.

### 6.3 OPERATION AND MAINTENANCE

Detailed operation and maintenance (O&M) requirements will be prepared as part of the design of the ground water treatment system. Major O&M requirements are identified below;

- Operational requirements for the treatment system include routine equipment checks, monitoring liquid and air flow rates, and sampling and analyses for influent and effluent water quality.
- the column internals will require a mild acid wash or removal and washing of the packing materials at least every 4 to 6 months to remove accumulated solids.
- The solids accumulated in the air-stripper wet well should be cleaned out once a year.



- The sludge generated from the precipitation step will be allowed to accumulate in the sludge holding tank. Due to the small quantity of sludge production, the sludge in the holding tank may be dewatered in the plant and frame filter press approximately once a week. The sludge cake can be sent to a sanitary landfill.
- The sludge holding tank, clarifier, sludge pumps and filter press will require periodic maintenance, similar to any small wastewater treatment system.

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TABLES

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TABLE 1: GROUND WATER ELEVATIONS (10/1 TO 10/14/88)

MILLCREEK (18-Jan-89)

a. Water Surface Elevations (ft amsl)



PUMPING CONDITIONS:<br>"Static" indicates static water levels (i.e. no wells being pumped); ""9,10" indicates well(s) pumped during water level measurements

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### WEATHER CONDITIONS DURING TREATABILITY TESTING (1988)

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COLUMN DIAMETER: 12 INCHES PACKING HEIGHT: 10 FEET PACKING MATERIAL: JAEGER TRI-PAK, 3" DIAMETER

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### MILLCREEK 01-Aug-89 TABLE 4: AIR STRIPPING PILOT TEST RESULTS Stripres.wkl



### b. AIR STRIPPED GROUND WATER CONCENTRATION (ug/l)



### LABORATORY QUALIFIERS:

J - denotes estimated value

D - indicates compound detected at secondary dilution

B - indicates compound detected in associated blank sample

E - value exceeds calibrated linear range of instrument

(1) Discharge limit proposed by USEPA in December 1987 technical evaluation.

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MILLCREEK 01-Aug-89

### TABLE 4: AIR STRIPPING PILOT TEST RESULTS

stripres.wk1

### (continued)

### PERCENT REMOVAL





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### TABLE 5

### AIR EMISSIONS FROM AIR STRIPPING COLUMN



Exposure limits from American Conference of Governmental Industrial Hygienists, 1988 Threshold Limit Values and NIOSH, Pocket Guide to Chemical Hazards, 1985.

ATG: Air Toxic Guidelines, Pennsylvania Department of Environmental Resources, Chapter 127, 1985.

Effluent Concentration:

Influent Concentration (ug/l) x 10<sup>-3</sup>  $\frac{mg}{ug}$  x 10<sup>-3</sup>  $\frac{1}{m}$ -3<sup>x</sup>  $\frac{1}{A \cdot W \text{ ratio}}$  (1 m<sup>3</sup>/60 m<sup>3</sup>)

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### NOTES:

SAMPLE VOLUME: 800 mis CARBON TYPES: Calgon 300 (Calgon Corp) Darco HD4000 (American Norit Co.) CONTROL SAMPLES: Control 0 received no carbon and no shaking Control 1 received no carbon Initial TOC concentration: Raw: 12 mg/l A.S.: 11.5 mg/l WATER SOURCE: Raw: Raw ground water from MW-9 and MW-10 A.S.: Airstripped ground water

BOD concentration in all samples was less than 2 mg/l.



\* - Sample GAC-0 represents mini-column influent concentrations

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Test Conditions:

-------------------------------Mini-column Diameter: 1/8-inch Carbon Bed Depth: 1.5-inches Mass Carbon in Bed: 0.31 grams

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NOTE: Sample GAC-0 represent mini-column influent

J - Denotes estimated value

D - Indicates compound detected at a secondary dilution

B - Indicates compound detected in associated blank

E - Value exceeds calibrated linear range of instrument



### Ce/Ci

\* - compound detected in mini-column effluent below

compound detected in mini-column errowshed buttlent<br>detection limit but not detected in column influent<br>ANO01202



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\* indicates supernatant sample submitted for TSS, total metal and dissolved metals analysis



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JAR TEST NUMBER: 4





\* indicates supernatant sample submitted for TSS, total metal and dissolved metals analysis

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indicates supernatant sample submitted for TSS, total metal and dissolved metals analysis

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### JAR TEST NUMBER: 7



Supernatant Sample ID: JT-7



JAR TEST NUMBER: 8





### MILLCREEK TABLE 12: JAR TEST RESULTS - SUPERNATANT SAMPLES FOR THE TABLE 12: JE-metal

### a. SUMMARY OF ANALYTICAL RESULTS



NOTE: Only values above the detection limit are reported. All concentrations are expressed in mg/l.

### b. PERCENT REMOVAL



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### RAW GROUND WATER

Initial pH: 6.8 s.u. Final pH: 9 s.u. Initial Turbidity: 1.30 NTU

### TURBIDITY (NTU)



### AIR STRIPPED GROUND WATER

Initial pH: 7.5 s.u. Final pH: 9 s.u. Initial Turbidity: 26.0 NTU

### TURBIDITY (NTU)



### NOTES:

Sample Volume: 5 gallons Temperature: Air: 9 C Water: 12 C pH adjusted to 9 s.u. using 20 ml of 10% Ca(OH)2 Polymer: Betz 1100 (0.05% solution) added to 5 ppm 28.4 ml sodium sulfide (1%) added to raw water sample only. Water pumped directly from MW-9 and MW-10 at a loading of 19 gpm/sf, A:W ratio 60:1. No interface noted in either sample during settling

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# TEST CONDITIONS:





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### TABLE 15

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### DESIGN PARAMETERS: GROUND WATER TREATMENT SYSTEM





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# KLA VERSUS LIQUID LOADING

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FIGURE 2c

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PACKING HEIGHT



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FIGURE 4

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CARBON ISOTHERMS

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FIGURE 5







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# TITRATION CURVE (1% CaOH2)

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FIGURE 8b

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meq added/liter

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 $\bullet$  $7.5$  $7<sup>1</sup>$  $\bullet$ 

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TITRATION CURVE (0.1N NaOH)

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#### **FIGURE IO**

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MILLCREEK, PENNSYLVANIA U.S. ARMY CORPS OF ENGINEERS

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SCHEMATIC OF<br>AROOI225<sup>LONG</sup> TUBE APPARATUS



GRAVITY THICKENING TEST



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APPENDIX A



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### APPENDIX A

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#### CITY OF ERIE SEWER DISCHARGE LIMITS

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#### CITY OF ERIE, PA

#### SPECIFIC POLLUTANT LIMITATIONS



(Not to exceed Average 24-hour concentration)

Reference: City of Erie, Ordinance 23-1984.

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# **APPENDIX B**

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#### APPENDIX B

#### VENDOR INFORMATION ON AIR-STRIPPER COLUMN SCALING AND PLUGGING

0285-23-1

#### MALCOLM PIRNIE, INC.

#### INTEROFFICE CORRESPONDENCE

Date: June 27, 1989

To: File: 0285-23-2, DRI

From: D. Daley-

Re: O&M Requirements - Air Stripping Tower Millcreek Superfund Site

Following is a summary of telephone conversations I had on June 23 with vendors/suppliers of air stripping towers and packing.

General Filter Co., D. J. Koester Associates (315) 637-9559 Mark Koester, Sales

General Filter recommends pretreatment of waters to remove iron to less than 0.5 mg/l to avoid fouling problems. The tower is available in either aluminum or stainless steel. Mark will call the manufacturer to find answer to questions about strength and frequency of acid wash, based upon design parameters I provided.

#### Jaeger Products. Inc. (800) 678-0345, Jerry Wingo

Jaeger recommends frequent (monthly) inspections of the packing to detect fouling or scaling problems early. Many installations are "reactionbased" O&M; that is, until the system is operating, it is difficult for one to anticipate all the maintenance requirements. No long-term, absolutely reliable maintenance technology is presently available. Jerry offered several options, namely:

- 2% HC1 (maximum strength) acid bath
- chlorine wash for bacteria problems
- strategically placed high pressure spray nozzles to blast off scale in place
- have extra packing material available to cycle the packing between uses

Purezone, Inc. (805) 758-4469, Bruce Greed, Rt1, Box 55, Wasco, CA 93280

Purezone has a proprietary process for which they are applying for "alternative technology" status from the USEPA. The cleaning process is presently in use at a hazardous waste site cleanup at Smith Kline-Beckman (1 MGD, 175 extraction wells). The system experienced problems with iron and manganese buildup. A 72-hour treatment is required to return the packing material to "like-new" condition. More information is being sent to me.

MALCOLM PIRNIE. INC.

#### TELEPHONE CALL CONFIRMATION



## D. J. Koester & Associates

7112 EAST GENESEE STREET, FAYETTEVILLE, N. Y. 130 (315) 637-9559 June 26, 1989 General Filter Company 600 Arrasmith Trail Ames, Iowa 50010-9761 Attn: Dale Watson cc: L.Ulhmeyer T.Lachcik Re: V.O.C. Removal D.Dailey file Dear Dale: We received a call recently from Malcolm Pirnie concerning a V.O.C. removal project. I am listing below the design parameters which they have given me. Design Flow 105 GPM (150,000 GPD)<br>Operation 24 hour continuous 24 hour continuous<br>12  $mg/L$ Raw Iron<br>Design TCE 100 micrograms per liter<br>1500 micrograms per liter Design 1,2 Dichloroethene<br>Design Vinylchloride 200 micrograms per liter<br>500 micrograms per liter 2 micrograms per liter<br>70 micrograms per liter

Design 1,1,1 Trichloroethane<br>Effluent TCE Effluent 1,2 Dichloroethene 70 micrograms per liter<br>Effluent Vinylchloride 2 micrograms per liter Effluent Vinylchloride Effluent 1,1,1 Trichloroethane 10 micrograms per liter<br>Design Loading Rate 10 30 GPM/sq.ft. Design Loading Rate

We need to provide recommendations for pretreatment, tower sizing and media selection. One area of major concern is that of ongoing maintenance. They are looking at the possibility of an acid wash periodically for the media. During my conversations with Les Ulhmeyer, he indicated that if pretreatment brought the iron level down to .5 mg/l or less, then cleaning of the media would not be an ongoing consideration and thus acid cleaning would not be necessary.

Although pretreatment would add to the initial capital cost, it appears that it would be the most economical route to go in the long run. If there is no pretreatment or it is not sufficient to reduce the iron to low enough levels, then the continual ongoing maintenance and media replacement would seem to be the most expensive route to go. We would like your comments concerning this.

Les had indicated that for pretreatment of the iron, you would propose a clarifier with the appropriate chemical feed. If they plan on pumping directly from the well into the tower, can we provide a pressure clarifier?

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Ref: V.O.C. Removal (6/26/89) Attn: Dale Watson

We would like to hear back from you concerning maintenance as soon as possible and at your earliest convenience for sizing, media selection, etc. We appreciate your assistance and look forward to hearing from you. Thank you.

Sincerely,

Mark Koester

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APPENDIX C

## COE COMMENTS ON DRAFT TREATABILITY TESTING REPORT

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U. S. Army Engineer District, Omaha Room 320, Executive Building 1624 Douglas Street Onaha, Nebraska, 68102

#### FACSIMILE COVER SHEET

TO: Malcolm Pirnie, INC. ATTN: Dharmja lyer S. 3515 Abbott Road Box 1938 Buffalo, New York 14219

FROM: USAGE Omaha District CPT Young

My Fax Phone # is: 402-221-7807 Please call me for confirmation, Voice 402-221-7844

DATE: 14 April 1989

Number of Pages to Follow: 6

Destination's Fax Phone # 716-828-0431

Notes: Dharmja: Please find enclosed comments from Omaha District and MRD technical review staff. I will need return<br>comments on these items. Please call me to set a date for items. Please call me to set a date for<br>CPT Young return comments.

TO: C. YOUNG

FROM: J.D. KOBLER

RE: REVIEW OF WATER TREATABILITY TESTING REPORT/MILLCREEK SUPERFUND SITE

DATE: FEBRUARY 21, 1989

I have reviewed the above-mentioned document prepared by Malcom Pirnie, Inc. in Draft (February 1989). It appears there is minimal contamination resulting from the Millcreek site making it difficult to justify a treatment plant in design. As stated on page 4, paragraph 3, of the document- "whether the ground water can be accepted without treatment needs to be evaluated." The A-E should develop this option in the text after presenting organic and inorganic study results.

Treatability Testing Report<br>
Remedial Clean-Up Treatability Study<br>
Remedial Clean-Up Treatability Study<br>
Submittal Mo.: C-997 Remedial Clean-Up Treatability Study<br>Millcreek Superfund Site

Request Date: 20 Mar 89

Request Date: 20 Mar 39<br>
CORPS OF ENGINEERS | TO: R. Hines | CENNING REVIEW COMMENTS l&i MM) CORPS OF ENGINEERS | TO: R. Hines<br>ENGINEERING REVIEW COMMENTS | CEMRD-ED-EA 1 **I** District • PLANS & SPECS AND/OR DESIGN REPORT | DESIGNED BY: | PROJECT: Treatability Study ! ! PRELIM IX {FINAL ! ! AS -ADV. 1JX1A E i IDIST 1 Millcreek Superfund Site 1 ! LOCATION OR BASE: 1 INVITATION NO.: CONTRACTOR: Erie, Pennsylvania ! \* DACA Malcolm Pirnie ł 1 COMMENTS BY: BRANCH OR SECTION: ī DATE: D. B. Taggart CEMRD-ED-GC 10 April 89 1 DRAWING f OR1 ITEM i | PHONED TO: Sheet  $1$  of  $1$  ! (NAME/DATE)  $\frac{1}{2}$  and  $\frac{1}{2}$  a General 1 There are an inadequate number of quality control samples reported (e.g. Table 4 lists no field quality control samples for volatiles), please report field quality control samples in Tables and discuss in the text. Page 4 2 Since total metals might exceed the City of Erie Ordinance 23-1984 requirements, these requirements should be listed in a table on page 4 or in the Appendix and discussed in the text. Page 6 3 The Report indicates two air-to-water ratios and five different liquid loadings. However, the actual work that was completed is different than the above. Please correct the text to reflect the actual work. Page 7 6 4 The text indicates an overall column height of 12 feet; Figure 1 shows 13 feet. This discrepancy should be clarified. Page 8 S S Were the temperature variations of the influent groundvater considered and accounted for in the data analysis? A brief statement of the expected significance is warranted on page 8. Page 8 6 The varied sampling times and modes of sample handling could result in incomparable results. Furthermore, the combination of discrete volatile samples is outside the provision of the QCP. Please explain fully how volatile samples were combined and the rationale for changes to the sampling protocol midway through the treatability study. Page 16 7 The conclusion that the organic carbon compounds present in groundvater samples are possibly semi-volatiles (e.g. base/neutral/acid extractables) is incorrect based on the Table 9 results. Please clarify.

#### Treatability Testing Report GC Log-in No.: 466 Remedial Clean-Up Treatability Study Submittal No.: C-997 Millcreek Superfund Site **Request Date: 20 Mar 89**

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#### Treatability Testing Report Remedial Clean-Up Treatability Millcreek Superfund Site Study

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GC Log-in No. 466 Su**bmittal No.:** C-997 Request Date: 20 Mar 89





Project: Millcreek Superfund Site Project Location: Erie, Pennsylvania

Comments By: David Reimer Branch/Section: Environmental (CEMRO-ED-DK)



#### CORPS OF ENGINEERS SHEET 2 OF 2<br>NEERING REVIEW COMMENTS DATE: 23 Feb. 1989 ENGINEERING REVIEW COMMENTS





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#### APPENDIX C

#### RESPONSES TO COMMENTS ON DRAFT TREATABILITY TESTING REPORT

#### COMMENTS BY J.D. KOBLER

MALCOLM PIRNIE

> We assume that Ms. Kobler's comment, "it appears there is minimal contamination resulting from the Millcreek site making it difficult to justify a treatment plant in design," pertains to the option of providing on-site treatment versus discharge to the sewer for treatment at the WWTP. The statement on page 4, paragraph 3 of the draft report - "whether the ground water can be accepted without treatment needs to be evaluated" was made since the option of direct discharge without treatment appeared to be viable at the time the draft report was prepared,k as the City did not have specific limits on volatile organic contaminants (VOCs).

> Meetings were held with the City of Erie, Town of Millcreek and USEPA subsequent to the preparation of the draft Treatability Testing Report. As detailed in a memorandum copied to Captain Young (May 10, 1989), the City was concerned about the potential risk of exposing the public to VOCs should untreated ground water be discharged to the sanitary sewers. Consequently, direct discharge to the sewers without treatment was eliminated as an option subsequent to the meeting. Section 1.3 has been modified accordingly.

> In addition, the City had indicated that the available sewer capacity in the vicinity of the site and the hydraulic capacity in the City of Erie Wastewater Treatment Plant (WWTP) were limited; additional capital costs would be required to provide for a discharge pipe from the ground water treatment facility to the nearest sewer, and for potential sewer capacity and WWTP hydraulic improvements. In summary, the selected treatment option is to provide on-site VOC and inorganics removal with direct discharge to Marshall's Run.

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COMMENTS BY D. B. TAGGART

- 1. Quality control samples were not required in the Scope of Services for the treatability testing. Samples collected during treatability testing were used for an evaluation of treatment techniques only and not for characterization of ground water; consequently QA/QC samples were not collected.
- 2. The City of Erie Ordinance 23-1984 sewer discharge limit for parameters of interest are included as Appendix A.
- 3. The report text reflects the fact that a total of 10 combinations of air-to-water ratios and liquid loadings were specified in the scope; actual air-to-water ratios ranged from 20:1 to 50:1 and the liquid loadings ranged between 19 and 40 gpm/sf.
- 4. The overall pilot air-stripper column height was 13 feet; the discrepancy between the text and Figure 1 has been corrected.
- 5. Water temperatures measured during the air-stripper pilot column runs were considered in the calculations for mass transfer coefficients (see Section 3.5.1). Henry's Law constants for column sizing are based on the lowest reported influent water temperature, while the mass transfer coefficients are based on a linear regression of the values calculated from pilot data at the applicable loading rates. The scatter in the calculated mass transfer coefficients is more due to experimental error than due to the variation in the influent water temperature during testing. The use of a tanker truck for temporary storage contributed largely to the variation in influent water temperature. Actual ground water temperature is expected to be relatively uniform (within 2"C) throughout the year. The 22-foot packing depth should therefore be sufficient for ground water treatment at the site.



6. The empty bed contact time in the pilot air-stripper varied between 2 and 4 minutes at the ground water flow rates (15 to 30 gpm) used in the testing. Based on these contact times and Malcolm Pirnie's experience with pilot air-stripping columns, equilibrium conditions should be attained within 15 minutes of the start of a column run. Samples collected after 15 minutes are therefore representative of the VOC removal efficiency of the column under the specific set of test conditions.

The method of compositing VOC samples was as follows: Discrete VOC samples were submitted to the lab in 40 ml-vials. Equal aliquots from each sample were withdrawn into a syringe until the desired total volume needed for the analysis was obtained. The syringe and purge vessel acted to mix the discrete aliquots to obtain a composite VOC analysis. The purge time was sufficiently long (11 minutes) to allow any VOCs present to be purged.

The samples for VOC analysis were initially composited at 15, 60 and 120 minutes after the start of each test, in accordance with the Work Plan. However, due to the concerns over the loss of volatile organics during the compositing of samples and any error that may be introduced in the mass transfer calculations resulting from the averaging of concentrations, the procedure was modified in the field to analyze only discrete samples. A review of the data shows little difference in water quality between discrete and composite influent samples. For 1,2 DCE, the influent composite samples ranged from 200 to 1300 ug/1, while the discrete samples ranged from 630 to 1200 ug/l. Similarly, TCE concentrations ranged from 9 to 15 ug/l for composite influent samples, and from 11 to 12 ug/l for discrete influent samples. These results indicate that neither the fact that samples were composited nor the different sampling intervals had any apparent influence on the water quality.

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- 7. Neither VOCs or semi-volatile organic compounds (viz. base/neutral/ acid/extractables) were present in sufficient concentrations to account for the measured organic carbon concentrations. We therefore agree that the organic compounds in the ground water samples are not due to semi-volatiles, but predominantly the result of naturally occurring fulvic and humic acids.
- 8. A bed depth of 1.5 inches is generally used by Malcolm Pirnie for GAC mini-column tests. In order to provide greater contact time and better breakthrough characteristics, the larger bed depth of 8 inches, which was not used before by Malcolm Pirnie on similar ground water, was attempted. Due to the characteristics of the ground water at the site and the size distribution of the pulverized GAC, high pressure drops were obtained at bed depths greater than 1.5 inches. A bed depth of 1.5 inches was used for the evaluation of GAC.
- 9. Chemical treatment of the ground water before the air-stripper is primarily for iron removal, which exist as the ferrous ion in the ground water. Ferrous sulfide is far more insoluble than ferrous hydroxide. Therefore, sodium sulfide was added prior to pH adjustment to allow the preferential formation of insoluble metal sulfides. Sodium sulfide also raises the pH, thereby requiring less lime or caustic to subsequently adjust the pH. The addition of sodium sulfide as a polishing step after pH adjustment and filtration will not result in a reduction in sulfide requirements, but may require another solids separation step.
- 10. A 0.4% sulfuric acid stock solution (normality 0.008N) was used for pH adjustment.
- 11. The sludge was shipped to two different vendors of dewatering equipment. One vendor returned the filter cake in a glass container; the other returned the filter cake in an airtight plastic bag. Rather than extensively disturb the sample and risk the additional

loss of VOCs just to place the sample in a 40 ml-vial, the dewatered sludge cakes were shipped intact to the lab for analysis.

- 12. For the VOCs which were removed to less than the detection limit in the column effluent, the removal efficiency is stated as greater than 99%  $(>99%)$ . This is justifiable since the quantitation limits for volatile organics are an order of magnitude lower than the instrument detection limits.
- 13. A total of twenty (20) VOC samples were budgeted for the pilot airstripper testing. The original Work Plan should have mentioned only twenty samples, not forty. This was later corrected in the Treatability Test Work Plan.
- 14. The equation for calculating different air concentrations in Table 5 has been corrected to show the inverse of the air-to-water ratio. The calculations shown in Table 5 were, however, performed correctly.
- 15. The quantitation limits for organics are generally an order of magnitude lower than reportable instrument detection limits. If the mass spectral data indicated the presence of a compound which meets the identification criteria but the concentration of that compound was below the detection limit, the laboratory reported the calculated concentrations with a "J" qualifier, signifying an estimated value. Compounds not detected by the GC or GC/MS are reported as less than the detection limit. The values in Table 9 are as reported by the laboratory for the water samples.
- 16. Although the calculated  $K<sub>i</sub>$  avalues in Figure 2a-2d are widely scattered, the values obtained from linear regression of the data at the desired liquid loading rates are consistent with those reported in the literature and Malcolm Pirnie's experience with similar packing material.

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## MALCOLM PIRNIE

## COMMENTS BY DAVID REIMER

- 1. The draft Treatability Testing Report was prepared and submitted to the COE in February 1989 after completion of the field testing, even though ground water flow modeling efforts to estimate hydraulic capacities for the ground water extraction system was incomplete. The items listed in Comment #1 were therefore not included in the Treatability Testing Report. A summary of the test results and recommended treatment system schematic has been added to this final Treatability Testing Report. The Engineering Report (June 1989) includes:
	- a summary of the treatability testing results;
	- a recommended treatment scheme with schematic;
	- preliminary cost estimate for construction, operation and maintenance; and
	- basis for design.
- 2. Other water quality standards are not of significant concern with respect to ground water and were not recommended by the USEPA.
- 3. See response to Comment No. 5 by D. B. Taggart.
- 4. A discussion on the potential for scaling and plugging of column internals is included in Section 3.5.
- 5. The air-stripping tower with 22-foot packing height will be adequate for ground water treatment. Two 20-foot air-strippers in series would provide capacity far in excess of what is required at this site. Since the ground water collection and treatment system can be shut down easily for a short period of time if necessary, with minimal contaminant release through ground water movement off-site, a backup air-stripper is not required.

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- 6. BOD tests were performed for all samples listed in Table 6 (24 samples for batch isotherm test) and Table 7 (5 samples for BAG minicolumn test) as required in the Scope of Services.
- 7. The clarifier loading rate is 1000 gpd/sf.
- 8. The principal inorganics of concern are iron and manganese. Both caustic and lime provided adequate removal of these inorganics prior to and subsequent to air-stripping. As lime is generally less costly than NaOH, and does not present as great a risk to treatment plant workers during handling as does caustic, lime was preferred for pH adjustment.

As the air-stripping process resulted in the formation of ferric hydroxide and raised the pH slightly, less chemical is required for pH adjustment following air-stripping. Therefore, the preferred order of treatment is air-stripping followed by pH adjustment, flocculation and settling.

9. The Engineering Report contains a complete evaluation of the treatability testing results and recommendations. The Treatability Testing Report has been incorporated into the Engineering Report.