

US EPA ARCHIVE DOCUMENT

# Environmental Technology Verification Report

## Evaluation of USFilter Membralox<sup>®</sup> Silverback<sup>™</sup> Model 900 Alkaline Cleaner Recycling System

Prepared by



Under a Cooperative Agreement with



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# Environmental Technology Verification Report

## Evaluation of USFilter Membralox<sup>®</sup> Silverback<sup>™</sup> Model 900 Alkaline Cleaner Recycling System

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## FOREWORD

The Environmental Technology Verification (ETV) Program has been established by the U.S. Environmental Protection Agency (EPA) to evaluate the performance characteristics of innovative environmental technologies for any media and to report this objective information to the states, local governments, buyers, and users of environmental technology. EPA's Office of Research and Development (ORD) has established a five-year pilot program to evaluate alternative operating parameters and to determine the overall feasibility of a technology verification program. ETV began in October 1995 and will be evaluated through September 2000, at which time EPA will prepare a report to Congress containing results of the pilot program and recommendations for its future operation.

EPA's ETV Program, through the National Risk Management Research Laboratory (NRMRL), has partnered with *CTC* under the Environmental Technology Verification Program P2 Metal Finishing Technologies Pilot (ETV-MF). The ETV-MF Pilot, in association with the EPA's Metal Finishing Strategic Goals Program, was initiated to identify promising and innovative metal finishing pollution prevention technologies through EPA supported performance verifications. The following report describes the verification of the performance of the USFilter Membralox<sup>®</sup> Silverback<sup>™</sup> Model 900 Alkaline Cleaner Recycling System for use in the metal finishing industry.

**ACRONYM and ABBREVIATION LIST**

$\Delta T$	Temperature Difference
$^{\circ}F$	Degrees Fahrenheit
Btu	British Thermal Unit
CTC	Concurrent Technologies Corporation
DI	De-ionized
D/P	Discharge/Permeate
EFF	Effluent
EPA	U.S. Environmental Protection Agency
ETV	Environmental Technology Verification
ETV-MF	Environmental Technology Verification Program P2 Metal Finishing Technologies
ft <sup>2</sup>	Square feet
gal	gallons
gpm	Gallons per minute
HDPE	High Density Polyethylene
HP	Horsepower
hrs/wk	hours per week
IDL	Instrument Detection Limit
IN	Influent
kWh	Kilowatt-hour
lb	Pound
L(l)	Liters
m <sup>2</sup>	square meters
mg/l	milligrams per liter
MDL	Method Detection Limit
mm	millimeters
MSDS	Material Safety Data Sheet
NRMRL	National Risk Management Research Laboratory
O&M	Operating and Maintenance
ORD	Office of Research and Development
P2	Pollution Prevention
psi	Pounds per square inch
QA	Quality Assurance
QA/QC	Quality Assurance/Quality Control
TSS	Total Suspended Solids

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## THE ENVIRONMENTAL TECHNOLOGY VERIFICATION PROGRAM



U.S. Environmental Protection Agency



Concurrent Technologies Corporation

### ETV VERIFICATION STATEMENT

<b>TECHNOLOGY TYPE:</b>	<b>MICROFILTRATION</b>		
<b>APPLICATION:</b>	<b>AQUEOUS CLEANING APPLICATIONS</b>		
<b>TECHNOLOGY NAME:</b>	<b>Membralox® Silverback™ Model 900</b>		
<b>COMPANY:</b>	<b>USFilter Corporation</b>		
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The United States Environmental Protection Agency (EPA) has created the Environmental Technology Verification Program (ETV) to facilitate the deployment of innovative or improved environmental technologies through performance verification and dissemination of information. The goal of the ETV Program is to further environmental protection by substantially accelerating the acceptance and use of improved, cost-effective technologies. ETV seeks to achieve this goal by providing high-quality, peer-reviewed data on technology performance to those involved in the design, distribution, financing, permitting, purchase, and use of environmental technologies.

ETV works in partnership with recognized standards and testing organizations, stakeholder groups consisting of buyers, vendor organizations, and states, with the full participation of individual technology developers. The program evaluates the performance of innovative technologies by developing test plans that are responsive to the needs of stakeholders, conducting field or laboratory tests (as appropriate), collecting and analyzing data, and preparing peer-reviewed reports. All evaluations are conducted in accordance with rigorous quality assurance protocols to ensure that data of known and adequate quality are generated and that the results are defensible.

The P2 Metal Finishing Technologies Program (ETV-MF), one of 12 technology focus areas under the ETV Program, is operated by Concurrent Technologies Corporation, in cooperation with EPA's National Risk Management Research Laboratory. The ETV-MF Program has evaluated the performance of a microfiltration technology for the recycling of alkaline cleaners. This verification statement provides a summary of the test results for the USFilter Membralox® Silverback™ Model 900 alkaline cleaner recycling system.



## VERIFICATION TEST DESCRIPTION

The USFilter Membralox® Silverback™ Model 900 (Silverback™ unit) was tested, under actual production conditions, on an alkaline cleaner, at Gates Rubber Company in Versailles, MO. Alkaline cleaning is performed on metal parts at different times during the manufacturing process to remove oils, coolants and other metalworking fluids prior to electroplating. The verification test evaluated the ability of the Silverback™ unit to remove oils and recover the alkaline cleaning chemistry.

Testing was conducted during two distinct 5-day test periods (Run 1 and Run 2):

- During the first test period (Run 1), the Silverback™ unit was operated at a typical oil and suspended solids loading rate for Gates Rubber Company operations.
- During the second test period (Run 2), the Silverback™ unit was operated at a significantly higher than normal oil and suspended solids loading rate.

Historical operating and maintenance labor requirements, chemical usage, and waste generation data were collected to perform the cost analysis.

## TECHNOLOGY DESCRIPTION

The Membralox® Silverback™ Model 900 is a microfiltration technology that is used to recycle alkaline cleaner. In operation, alkaline cleaner contaminated with oil, enters a two-compartment stainless steel tank through a prefilter that removes large particulate material from the feed stream. Free oil accumulates in the initial compartment and can be removed on a periodic basis through a drain port located on the upper part of the tank. The liquid then moves to a second tank compartment through a sub-surface passage; thereby leaving the floating oils in the first compartment. The liquid in the second compartment (referred to as the recirculation tank) is pumped through a microfiltration ceramic filter (0.2  $\mu$ ). The filter reject returns to the recirculation tank and the recovered alkaline cleaner flows back to the cleaning process. At Gates Rubber Company, the Silverback™ unit recovers 1.0 gpm of alkaline cleaner.

## VERIFICATION OF PERFORMANCE

24 hour composite samples were collected from the feed to the Silverback™ unit and the recovered cleaner from the Silverback™ unit daily during each test. In addition, a 5% solution of the concentrated cleaner was made and analyzed for comparison purposes.

Average analytical results for key parameters are shown in Table 1. Total solids is a measure of all dissolved and suspended solids in the samples. Alkaline components and dipropylene glycol ether are the key inorganic and organic ingredients of the alkaline cleaner. Total suspended solids and oil are the contaminants being removed during the recovery process. The recovered alkaline cleaner is similar in composition to the unused cleaning solution with regard to its key organic ingredient (dipropylene glycol ether), but significantly higher regarding total solids and alkalinity.



**Energy Use.** Energy requirements for operating the Silverback™ unit at Gates Rubber Company include electricity for the system pump and steam (from a natural gas fired boiler) for reheating the recovered alkaline cleaner for re-use in the cleaning process. Electricity use was determined to be 134.3 kWh/day, based on continuous use of the system. The energy requirement for reheating the recovered alkaline cleaner is 271,000 BTUs/day. The amount of natural gas required to generate this quantity of energy is approximately 2.71 therms/day.

**Waste Generation.** A waste generation analysis was performed using current operational data and historical records from the Gates Rubber Company. Implementation of the Membralox® Silverback™ Model 900 has reduced the disposal frequency of the alkaline cleaning solution from 15 times per year to two times per year. The overall volume of concentrated waste generated from alkaline cleaning has been reduced by 67.5% and the weight of total solids in the waste products has been reduced by 58.9%.

**Operating and Maintenance Labor.** Operating and maintenance (O&M) labor requirements for the Membralox® Silverback™ Model 900 were monitored during testing. The O&M labor requirement for the equipment was observed to be 3.75 hrs/wk. O&M tasks performed during the verification test include daily inspections of the unit and weekly cleaning of the tank and membrane.

**Cost Analysis.** A cost analysis of the Membralox® Silverback™ Model 900 was performed using current operating costs and historical records from the Gates Rubber Company. The installed capital cost (1999) of the unit was \$43,000 (includes \$36,000 for the unit, \$5,000 for storage tanks, and \$2,000 for installation costs). The annual cost savings associated with the unit is \$32,064. The projected payback period is 1.3 years.

## SUMMARY

The test results show that the Membralox® Silverback™ Model 900 provides an environmental benefit by extending the bath life of the alkaline cleaner, thereby reducing the amount of liquid and solid wastes produced by the cleaning operation without removing the cleaning constituents of the bath. The economic benefit associated with this technology is low operating and maintenance labor and a payback period of approximately 1.3 years. As with any technology selection, the end user must select appropriate cleaning equipment and chemistry for a process that can meet their associated environmental restrictions, productivity, and cleaning requirement.

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**NOTICE:** EPA verifications are based on evaluations of technology performance under specific, predetermined criteria and appropriate quality assurance procedures. EPA and CTC make no expressed or implied warranties as to the performance of the technology and do not certify that a technology will always operate as verified. The end user is solely responsible for complying with any and all applicable federal, state, and local requirements. Mention of commercial product names does not imply endorsement.

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## 1.0 INTRODUCTION

The Membralox® Silverback™ Model 900 (Silverback™ Unit) is a microfiltration system for recycling used alkaline cleaning solutions (cleaners). Alkaline cleaning is performed on metal parts at different times during the manufacturing process to remove oils, coolants and other metalworking fluids prior to electroplating. The verification test evaluated the ability of the Silverback™ unit to remove oils and recover the alkaline cleaning chemistry. It was tested by CTC under the U.S. Environmental Protection Agency (EPA) Environmental Technology Verification Program for P2 Metal Finishing Technologies (ETV-MF). The purpose of this report is to present the results of the verification test.

The Silverback™ Unit was tested to evaluate and characterize the operation of the microfiltration system through measurement of various process parameters. Testing was conducted at Gates Rubber Company located in Versailles, MO. Gates Rubber Company manufactures a wide range of hydraulic couplings and hose assemblies.

## 2.0 DESCRIPTION OF ALKALINE CLEANER RECYCLING SYSTEM

### 2.1 Alkaline Recycling Equipment

A diagram of the Silverback™ Unit is shown in **Figure 1**. In operation, the contaminated cleaner enters a two-compartment, type 304 stainless steel tank through a filter (polypropylene sock and stainless steel basket) that removes large particulate material from the feed stream. The level in the tank is maintained by a level switch, which controls the tank inlet valve and also acts as a low-level cutoff for the system pump. Oils may accumulate in the initial compartment (referred to as the settling tank) and can be removed on a periodic basis through a drain port located on the upper part of the tank. The liquid then moves to a second tank compartment through a sub-surface passage, leaving any floating oils in the first compartment. The liquid in the second compartment (referred to as the recirculation tank) is pumped through the ceramic membrane located in the microfiltration module. A portion of the water and cleaner chemicals are forced through the ceramic membrane and exit the system to a permeate holding tank, while a portion of the water and cleaner chemicals are retained, along with oil and suspended solids and recycled back to the recirculation tank. Periodically, the liquid in the recirculation tank is discarded and the tank and ceramic membrane are cleaned. The operating cycle used at Gates Rubber Company is described in Section 2.3

This Silverback™ Unit contains a Membralox® 7P19-40 filtration module consisting of seven  $\alpha$ -alumina elements, each with 19 lumens (channels) that are 4.0 mm in diameter. The inside of each channel is lined with an  $\alpha$ -alumina or zirconia membrane having a total surface area of 1.68 m<sup>2</sup> (18.1 ft<sup>2</sup>) and a pore size of 0.2  $\mu$ m.

The Silverback™ Unit is equipped with an air-driven, backpulsing device that is designed to clean the filtration modules during operation by periodically pushing solution, under pressure, in a direction opposite to that used for normal filtration. The frequency and duration of the backpulse cycle is controlled by a timer. During each backpulse, a volume



of approximately 700 ml of permeate is pushed through the ceramic membranes in about one tenth of a second. The unit then returns to its normal flow pattern.

Utility requirements for installation of the Membralox® Silverback™ Model 900 include:

- Instrument air: <1 scfm, 80 psi, dry, oil-free
- Electricity: 460 VAC, 60 Hz, three-phase
- Heat (optional): steam, 6 lb/hr or hot water 160 °F.

## 2.2 Test Site Installation

USFilter selected Gates Rubber Company, located in Versailles, MO, as the test site for verification testing of the Silverback™ Unit. The unit that was evaluated during this ETV-MF project was installed in September, 1999. However, Gates Rubber Company has previous experience with the Membralox® Silverback™ technology dating back to 1997.

Gates Rubber Company manufactures a wide range of hydraulic couplings and hose assemblies. They have a 115,000 ft<sup>2</sup> manufacturing facility. Alkaline cleaning is performed at various points in the plant. There are 12 in-process, cleaning tanks present in areas such as machining. Eleven of these units hold 40 gallons of alkaline cleaner and one holds 75 gallons. The largest cleaning operation is located on the barrel plating (zinc) line, where there is an 1,800 gallons soak cleaning tank and an 1,800 gallons electrocleaning tank. The 12 in-process cleaning tanks and the soak cleaning tank are plumbed into the cleaner recycling system that was tested during this project. The electrocleaning tank is serviced by a separate recycling system that was not tested.

The predominant oil found on the parts processed through the cleaning systems is a cutting oil (Premium Oil Company Tru Cut 2582). The Material Safety Data Sheet (MSDS) for this product indicates it is a petroleum-based hydrocarbon with additives. Its hazardous components are hydrotreated, light naphthenic oils and hydrotreated, heavy naphthenic oils. Laboratory analyses revealed that it is a mixed base, mineral oil that contained an ester-based additive and a phenolic antioxidant. Traces of cellulose, or a derivative thereof, were also present.

A diagram of the cleaner recycling system involved in this ETV-MF project is shown in **Figure 1**. The solution that is processed by the Silverback™ Unit comes from three sources, including the soak cleaning tank and drag-out rinse tank on the zinc plating line, and from in-process washers located in various parts of the manufacturing facility. Each of these three sources is connected by piping (represented by lines with arrows in **Figure 1**) to the storage tank. The overall volume of cleaning solution in the cleaning and storage tanks is 3,600 gallons.

The solution conveyed from in-process cleaning and the soak cleaning tank is used alkaline cleaner. The solution conveyed from the drag-out rinse tank to the storage tank is rinse water that contains alkaline cleaner. De-ionized (DI) water is added to the drag-out rinse tank from spray bars located above the drag-out rinse tank. The addition of this water



causes the solution in this tank to overflow a weir and the overflow is conveyed to the storage tank. The DI water sprays are automatically activated when a barrel is removed from the drag-out rinse tank. At Gates Rubber Company, the volume of water added by the sprays is balanced by evaporative losses from the hot alkaline cleaning tank.

The overall volume of solution in the alkaline cleaning system does not vary appreciably from day to day. By sending the overflow of the drag-out rinse tank to the recovery process, the alkaline cleaning system is operated in a closed-loop mode; i.e., no wastewater is generated from rinsing of the alkaline cleaner. However, some solution from the drag-out tank is retained on the barrels, racks, and parts as they exit the drag-out tank. This liquid, which is diluted cleaning solution, is conveyed to the electrocleaning process tank, which is the next tank in the plating sequence. The chemistry of the electrocleaning bath is similar to the alkaline cleaning bath chemistry (the electrocleaning bath has a higher concentration of chemical constituents). Therefore, the drag-out from the alkaline cleaning/rinsing process is assimilated into the electrocleaning process.

The solution in the storage tank flows by gravity to the Silverback™ Unit and is processed at a rate of approximately 1.0 gallon per minute (1400 gallons per day). The recovered product from the Silverback™ Unit is pumped to a recovered permeate tank. It is drawn off and reused in the soak clean tank and in-process washers.

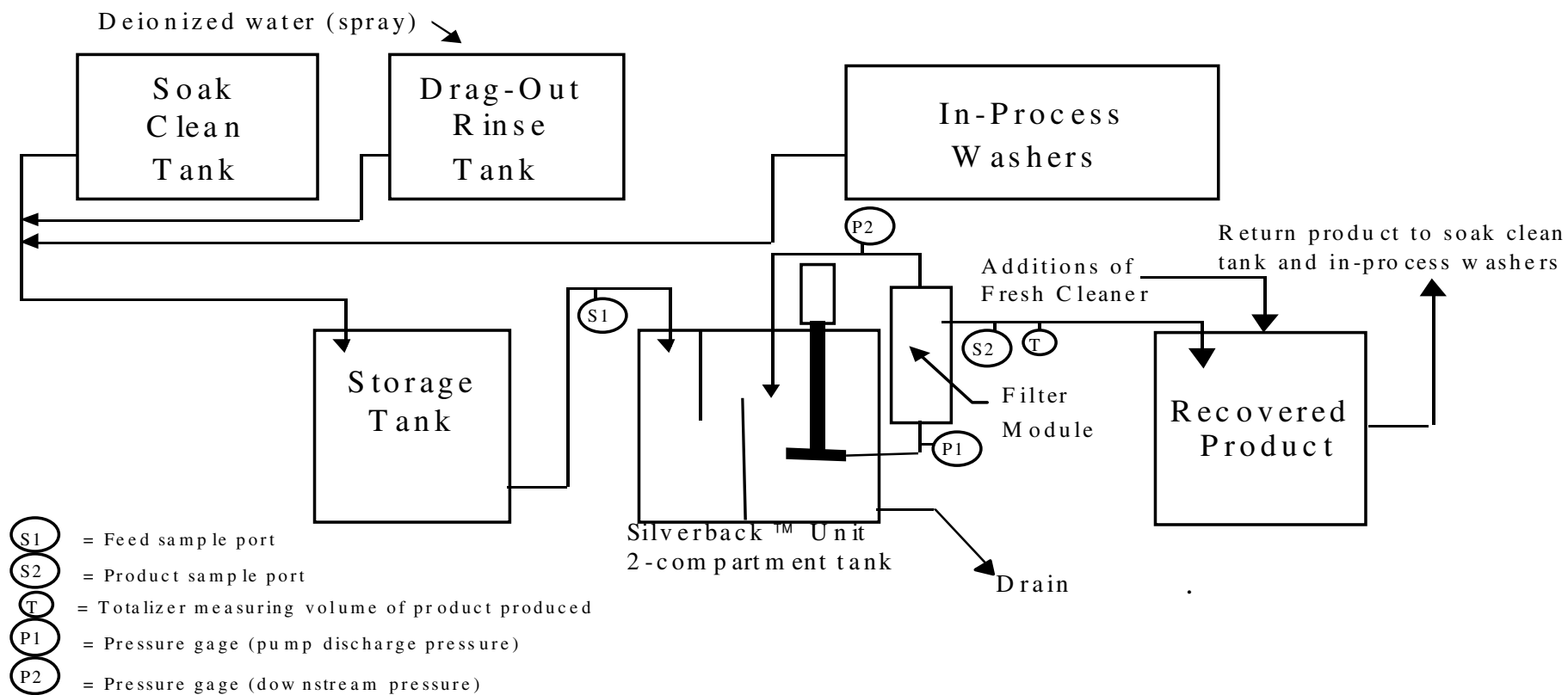


Figure 1. Alkaline Cleaner Recycling at Gates Rubber Company

Barrels exiting the drag-out rinse tank are further processed in an electrocleaning tank and subsequently zinc plated. As mentioned earlier, the electrocleaning tank is not connected to the recovery system being tested during this project.

The alkaline cleaner used at this facility is CLEAN-R-120GR, which is formulated and sold by PAVCO, a company located in Cleveland, Ohio. The MSDS for this product can be found in the test plan (Ref. 1). The concentration of the cleaner is controlled based on alkalinity concentration, which is determined by a titration method performed by the system operators. The CLEAN-R-120GR is purchased as a single-component, concentrated liquid. When measurements indicate that the alkalinity concentration is below a recommended operating level, additional liquid concentrate is added to the cleaning system.

On a semi-annual basis, the alkaline cleaning system (3,600 gallons) is drained and the solution is treated on-site. The system is then recharged with fresh chemistry (5% concentrated cleaner and 95% DI water). This recharging procedure is performed during maintenance periods in December and July.

### 2.3 Operating Cycle

An operating cycle of the Silverback™ Unit consists of four steps:

1. **Startup.** Recirculation tank is filled with DI water. The recirculation pump is activated and run for five minutes to ensure membrane is fully wetted. The unit is drained. The feed line valve is opened and alkaline cleaner from the storage tank enters the unit. A level switch controls the solution level in the unit and stops the incoming flow at a preset point. The system pump is activated causing solution to circulate through the filter module. After five minutes the permeate outlet valve is opened to start flow to the recovered permeate tank. The unit is now in service mode.
2. **Service.** Solution is pumped through the filter module. Recovered solution exits through the permeate outlet valve to the recovered permeate tank at a rate of 1 gpm. The tank feed valve is automatically opened and closed by the level switch based on the level in the recirculation tank. Every five minutes a backpulse occurs for 0.1 seconds. During the backpulse, the permeate outlet valve is automatically closed and the flow is reversed so that permeate is pushed back through the membrane. After each backpulse, the unit returns to its normal flow pattern. Operators periodically check the permeate flow rate and adjust the rate, if necessary, to maintain a 1.0 gpm flow rate.
3. **Shutdown.** The recirculation pump is shut down and the permeate outlet valve is closed.
4. **Cleaning.** The unit is completely drained. At Gates Rubber Company, this solution (100 gallons) is placed into a storage tank and subsequently treated on-site. The unit is filled with DI water and the recirculation pump is activated. Four gallons

of CLEAN-R-120GR are added to the water in the unit. The recirculation pump is activated for 1 hour. The unit is drained and refilled with DI water. One quart of 35% hydrogen peroxide is added to the unit. The recirculation pump is activated for one hour. The unit is drained and refilled with DI water. Four gallons of hydrochloric acid are added to the unit and the resulting solution is recirculated for 30 minutes. The unit is drained. This completes one operating cycle and the startup procedure is implemented to initiate another cycle.

At Gates Rubber Company, the recovery unit is operated on a one-week cycle. This time period was selected out of convenience and does not necessarily reflect the required frequency of cleaning. The Silverback™ Unit operating manual suggests that users monitor the input and output pressures of the membrane to determine when the unit requires cleaning. The pump discharge pressure (D) is read from an indicator located on the manifold piping, and the permeate pressure (P) is read from a indicator located on the membrane element. The Discharge/Permeate (D/P) ratio is used as a measure of flow resistance. When a high D/P ratio is experienced, the unit requires cleaning. The limiting D/P ratio varies from site to site, depending on factors such as cleaner and soil characteristics. The optimal D/P ratio for each site can be determined through operating experience.

### 3.0 METHODS AND PROCEDURES

#### 3.1 Test Objectives

The following is a summary of project objectives. Under normal system operating setpoints for the installation at Gates Rubber Company and varying contaminant-loading rates:

- Prepare a material balance for certain alkaline cleaner constituents and soils in order to:
  1. Evaluate the ability of the Silverback™ Unit to recover alkaline cleaner.
  2. Evaluate the ability of the Silverback™ Unit to remove contaminants from used cleaning solution.
- Determine the cost of operating the alkaline cleaning recovery system for the specific conditions encountered during testing by:
  1. Determining labor requirements needed to operate and maintain the Silverback™ Unit.
  2. Determining the quantity of energy consumed by the Silverback™ Unit during operation.
  3. Determining other costs associated with operation of the Silverback™ Unit.
- Quantify the environmental benefit performing an analysis of waste generation, which compares the quantity of waste generated before and after the installation of the Silverback™ Unit.

## 3.2 Test Procedure

### 3.2.1 System Set-Up

Prior to testing, the recirculation tank was drained and cleaned and the membrane was cleaned according to the manufacturer's instructions (Ref. 1). The recirculation tank was then filled with spent cleaner solution from the storage tank and the Silverback™ Unit was started. Sampling proceeded, once the unit was operating, with a permeate flow rate of 1.0 gpm. This flow rate is the target operating rate used by Gates Rubber Company.

### 3.2.2 Testing

The Silverback™ Unit was tested in accordance with the verification test plan (Ref. 1). Testing was conducted during two distinct, five-day test periods:

- During the first test period (Run 1), the unit was operated under the normal production conditions at Gates Rubber Company. At the completion of Run 1, the recirculation tank, which holds the soil removed from the alkaline cleaning solution, was drained from the recovery unit and stored for later use in Run 2.
- During the second test period (Run 2), the recovery unit was operated under normal production conditions, with one exception. To evaluate the operation of the recovery unit under a high soil loading condition, the recirculation tank solution that was removed and stored during Run 1 was introduced into the storage tank that feeds the cleaner recovery system at a uniform rate during the entire second test period. This procedure significantly increased the soil loading on the recovery unit during Run 2.

Sampling and process measurements were taken according to the schedule presented in **Table 1**.

As indicated in Section 2.2, the alkaline cleaning system is completely drained and recharged with fresh solution approximately every 180 days (two times per year). Test runs 1 and 2 were initiated 98 days and 120 days, respectively, after the system was recharged with fresh solution. Therefore, during this project, all testing was conducted during the 3<sup>rd</sup> quarter of the semi-annual operating cycle.

<u>Test</u>	<u>Test Objectives</u>	<u>Test Measurements</u>
Run 1 (baseline): Normal soil loading rate.	Prepare a material balance for alkaline cleaner constituents and soils.	Processing rate of solution through unit. Chemical characteristics of feed solution. Chemical characteristics of recovered permeate. Volume and chemical characteristics of wastes removed from two-compartment tank. Quantity of concentrated cleaning solution added during testing. Chemical characteristics of concentrated cleaning solution.
	Evaluate the ability of the Silverback™ Unit to process used alkaline cleaner solution and separate usable cleaner solution chemistry from bath contaminants.	Chemical characteristics of feed solution. Chemical characteristics of recovered permeate. Chemical characteristics of the waste products.
	Determine the alkaline cleaner recovery rate of the system, normalized based on production throughput and soil loading.	Volume of permeate produced. Production throughput for all associated cleaning baths. Chemical characteristics of feed solution. Chemical characteristics of recovered permeate.
	Determine labor requirements needed to operate and maintain the Silverback™ Unit.	O&M labor required during test period.
	Determine the quantity of energy consumed by the Silverback™ Unit during operation.	Quantity of energy used by pumps and filtration module. Quantity of energy used to reheat solution after recovery.
	Determine the cost of operating the alkaline cleaning recovery system for the specific conditions encountered during testing.	Costs of O&M labor, materials, and energy required during test period. Quantity and price of fresh cleaning chemicals added during testing.
	Quantify/identify the environmental benefit.	Review historical waste disposal records and compare to current practices.
Run 2. High soil loading Rate: approximately two times the normal soil loading rate.	Same objectives as Run 1.	Same measurements as Run 1.

**Table 1. Test Objectives and Related Test Measurements Conducted During the Verification of the Membralox® Silverback™ Model 900**

### 3.3 Quality Assurance/Quality Control

#### 3.3.1 Data Entry

Sampling events, process measurements, and all other data were recorded by the ETV-MF Project Manager on a pre-designed form (Ref 1).

#### 3.3.2 Sample Collection and Handling

Prior to the verification test, sampling ports were installed on the feed (IN) and permeate (EFF) lines of the Silverback™ Unit. Polyethylene tubes were connected to these two sampling ports and directed into 2.5-gallon, HDPE containers. During sampling, the sample collection containers were kept cool by placing them in a cooler containing ice.

The feed and permeate samples were collected in the HDPE containers at a continuous, uniform rate of approximately 5 to 8 ml/min (controlled by valve on sample ports) for 24-hour periods (i.e., 0700 hr to 0700 hr the next day). At the end of each 24 hr. sampling period, the HDPE containers were labeled and stored in a cooler containing ice, awaiting shipment to the analytical laboratory.

A grab sample from the recirculation tank was collected at the end of each test run. A sample of the proprietary cleaner (CLEAN-R-120GR) was collected from its original shipping container. These samples were labeled and stored prior to shipment in a cooler containing ice.

Samples shipped to the analytical laboratory were packed in coolers containing "blue ice". A two-day express service was used. All shipments were accompanied with chain of custody forms.

#### 3.3.3 Calculation of Data Quality Indicators

Data reduction, validation, and reporting were conducted according to the verification test plan (Ref. 1) and the ETV-MF Quality Management Plan (Ref. 2). Calculations of data quality indicators are discussed in this section.

##### 3.3.3.1 Precision

Precision is a measure of the agreement or repeatability of a set of replicate results obtained from duplicate analyses made under identical conditions. To satisfy the precision objectives, the replicate analyses must agree within defined percent deviation limits, expressed as a percentage, calculated as follows:

$$\text{RPD} = \left\{ \frac{|X_1 - X_2|}{\frac{(X_1 + X_2)}{2}} \right\} \times 100 \%$$

where,  $X_1$  = larger of the two observed values;

and  $X_2$  = smaller of the two observed values.

The analytical laboratory performed a total of 38 precision evaluations. All of the results were within the selected precision limits (Ref. 1) (within 30%). The results of the precision calculations are summarized in **Appendix A**.

### 3.3.3.2 Accuracy

Accuracy is a measure of the agreement between an experimental determination and the true value of the parameter being measured. Analyses with spiked samples were performed to determine percent recoveries as a means of checking method accuracy. The perfect recovery, expressed as a percentage, is calculated as follows:

$$P = \left[ \frac{(\text{SSR} - \text{SR})}{\text{SA}} \right] \times 100 \%$$

where:

SSR = spiked sample result; SR = sample result (native); and

SA = the concentration added to the spiked sample.

Quality Assurance (QA) objectives are satisfied for accuracy if the average recovery is within selected goals. The analytical laboratory performed 17 accuracy evaluations. All results were within the selected limits (Ref 1) (within 80-120% except for oil, which is within 50-150%). The results of the accuracy calculations are summarized in **Appendix B**.

### 3.3.3.3 Completeness

Completeness is defined as the percentage of measurements judged to be valid compared to the total number of measurements made for a specific sample matrix and analysis. Completeness, expressed as a percentage, is calculated using the following formula:

$$\text{Completeness} = \frac{\text{Valid Measurements}}{\text{Total Measurements}} \times 100\%$$



QA objectives are satisfied if the percent completeness is 90 percent or greater. All measurements made during this verification project were determined to be valid and completeness was 100%. Therefore the completeness objective was satisfied.

#### 3.3.3.4 Comparability

Comparability is a qualitative measure designed to express the confidence with which one data set may be compared to another. Sample collection and handling techniques, sample matrix type, and analytical method all affect comparability. Comparability was achieved during this verification test by the use of consistent methods during sampling and analysis and traceability of standards to a reliable source.

#### 3.3.3.5 Representativeness

Representativeness refers to the degree to which the data accurately and precisely represent the conditions or characteristics of the parameter represented by the data. For this verification project, three identical split samples (individual grab samples were split in the field) were sent to the laboratory for analysis.

The results of these samples are shown in **Appendix C**.

#### 3.3.3.6 Sensitivity

Sensitivity is the measure of the concentration at which an analytical method can positively identify and report analytical results. The sensitivity of a given method is commonly referred to as the detection limit. Although there is no single definition of this term, the following terms and definitions of detection were used for this project.

- **Instrument Detection Limit (IDL)** is the minimum concentration that can be differentiated from instrument background noise, that is, the minimum concentration detectable by the measuring instrument.
- **Method Detection Limit (MDL)** is a statistically determined concentration. It is the minimum concentration of an analyte that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero, as determined in the same or a similar sample matrix. In other words, this is the lowest concentration which can be reported with confidence. It may be determined by an IDL. The MDL's for this verification project are shown in **Table 2**.

Analyte	Units	Method Number	Method Reference	Method Detection Limit
Alkalinity (as CaCO <sub>3</sub> )	mg/l	2320B	SM	1.0
Carbonate-Alkalinity (as CaCO <sub>3</sub> )	mg/l	2320B	SM	1.0
Bicarbonate-Alkalinity (as CaCO <sub>3</sub> )	mg/l	2320B	SM	1.0
Hydroxide Alkalinity	mg/l	2320B	SM	1.0
Ammonia Nitrogen	mg/l	350.1	EPA	0.005
Total Nitrogen (TKN)	mg/l	351.3	EPA	0.25
Total Phenol	mg/l	420.2	EPA	0.005
Total Suspended Solids	mg/l	160.2	EPA	1.0
Total Solids	mg/l	160.3	EPA	1.0
Phosphate (as P)	mg/l	200.7	EPA	0.01
Dipropylene Glycol Ether	mg/l	GC/FID (see Appendix E)	N/A	1.0
Oil	mg/l	8015 modified	SW-846	0.2

Notes for Table 2: SM = Standard Methods for the Examination of Water and Wastewater, 18<sup>th</sup> ed.; EPA = Methods for Chemical Analysis of Water and Wastes, 1983; GC/FID = gas chromatography/flame ionization detector.

**Table 2. Laboratory Methodology Information**

#### 4.0 VERIFICATION DATA

##### 4.1 Analytical Results

A complete summary of analytical data is presented in **Table 3**. The samples coded "IN" are 24-hr composite samples of the feed to the recovery unit, and those coded "EFF" are 24-hr composite samples of the recovered permeate. Average values calculated for both the IN and EFF samples are also shown. The R-1 and R-2 samples are grab samples from the recovery tank, collected at the end of the test Runs 1 and 2. The "CLEANER" sample is a grab sample of the unused concentrated cleaner. The values for "5% of CLEANER" were calculated by multiplying the CLEANER results by 5%. These values approximate

the concentration of these constituents in a freshly formulated alkaline cleaner bath (i.e., the alkaline cleaning solution at Gates Rubber Company is formulated with a 5% solution).

The primary contaminants of the alkaline cleaning solution are total suspended solids and oil. The values for these parameters during Run 1 represent normal production conditions. During Run 2, adding a concentrated, soiled solution to the feed stream intentionally increased the concentration of these contaminants (see description of procedure in section 3.2.2). This procedure simulated a higher soil loading condition than during Run 1.



	Total Alkalinity mg/l as CaCO3	Carbonate Alkalinity mg/l as CaCO3	Bicarbonate Alkalinity mg/l as CaCO3	Hydroxide Alkalinity mg/l as CaCO3	Dipropylene Glycol Ether mg/l	Ammonia Nitrogen mg/l	Total Nitrogen (TKN) mg/l	Total Phenol mg/l	Total Suspended Solids mg/l	Total Solids mg/l	Phosphate (as P) mg/l	Oil mg/l
<b>Run 1</b>												
IN-1	2,700	1,300	650	<1	6,200	2.8	2.8	0.59	100	9,600	400	100
EFF-1	2,500	1,300	640	<1	6,300	3.7	3.8	0.63	24	9,100	390	19
IN-2	2,600	1,400	680	<1	6,200	3.1	4.3	0.57	170	9,600	390	180
EFF-2	2,500	1,300	670	<1	6,100	4.1	4.5	0.54	30	7,600	380	16
IN-3	2,600	1,200	620	<1	6,400	0.97	3	0.58	180	9,600	390	76
EFF-3	2,600	1,400	680	<1	6,200	3.5	23	0.42	48	9,200	390	18
IN-4	2,600	1,300	670	<1	6,100	1.1	7.2	0.05	160	9,500	390	200
EFF-4	2,600	1,400	680	<1	6,300	3.3	3.6	0.16	66	9,100	380	17
IN-5	2,400	1,100	550	<1	5,900	2.6	12	0.05	210	8,400	350	180
EFF-5	2,400	1,100	560	<1	6,300	2.7	3.2	0.062	92	8,500	350	51
IN-RUN 1 AVG	2,580	1,260	634	<1	6,160	2.1	5.9	0.4	164	9,340	384	147
EFF-RUN 1 AVG	2,520	1300	646	<1	6,240	3.5	7.6	0.4	52	8,700	378	24
R-1	3,300	1,200	620	<1	6,900	11	68	0.52	10,000	16,000	800	5,000
<b>Run 2</b>												
IN-6	2,200	1,000	560	<1	6,400	2.1	37	0.5	590	11,000	410	440
EFF-6	1,900	1,000	480	<1	6,400	0.023	37	0.57	1	10,000	320	21
IN-7	2,100	1,100	520	<1	5,700	1.9	43	0.7	910	11,000	490	1,000
EFF-7	2,000	1,100	500	<1	4,650	0.088	35	0.63	23	10,000	310	17
IN-8	2,600	1,100	540	<1	5,100	1.4	36	0.61	400	9,600	420	620
EFF-8	2,600	1,300	630	<1	5,100	0.025	39	0.58	4	9,300	360	13
IN-9	2,500	1,200	600	<1	5,200	2	26	0.57	180	8,900	420	530
EFF-9	2,200	1,000	520	<1	4,850	0.032	33	0.54	6	8,300	400	18
IN-10	2,300	1,000	500	<1	4,500	1.3	6.7	0.47	170	10,000	320	710
EFF-10	2,300	940	470	<1	4,500	0.078	0.49	0.19	35	11,000	340	23
IN-RUN 2 AVG	2,340	1,080	544	<1	5,380	1.7	29.7	0.6	450	10,100	412	660
EFF-RUN 2 AVG	2,200	1,068	520	<1	5,100	0.049	28.9	0.5	14	9,720	346	18
R-2	3,900	1,000	520	<1	5,200	3.4	44	0.95	6700	85,000	990	16,000
CLEANER	23,000	3,000	15,000	6,400	118,000	0.024	0.25	1.5	100	80,000	310	470
5% of CLEANER	1,150	150	750	320	5,900	0.0012	0.0125	0.075	5	4,000	15.5	23.5

Table 3. Summary of Analytical Results

## 4.2 Process Measurements

Certain process measurements were taken on a daily basis during verification testing. These data have been consolidated and are summarized in **Table 4**. Solution temperature measurements were taken using a hand-held digital thermometer. The pump discharge pressure was read from a gauge located on the Silverback™ Unit's manifold piping, and the permeate pressure was read from a gauge located on the membrane element.

Test Run/ Sample Date	Total Permeate Volume, gallons	Temperature Recirculation Tank, °F	Temperature Recovered Permeate Tank, °F	Temperature Soak Clean Tank, °F	Pump Discharge Pressure psi	Permeate Pressure psi
<b>Run 1</b>						
5-22-00	1,509	118.8	111.8	133.7	52	26
5-23-00	1,496	127.4	115.4	141.0	52	24
5-24-00	1,405	126.5	117.5	139.5	52	24
5-25-00	1,361	123.5	112.5	154.0	52	21
5-26-00	1,352	122.4	113.0	142.2	52	18
<b>Total/Avg.*</b>	<b>7,123</b>	<b>123.7</b>	<b>114.0</b>	<b>142.1</b>	<b>52</b>	<b>23</b>
<b>Run 2</b>						
6-12-00	1,442	114.8	111.6	146.9	53	26
6-13-00	1,394	131.2	114.2	141.3	52	25
6-14-00	1,383	130.7	112.0	145.8	53	23
6-15-00	1,382	125.3	90.7	142.0	52	20
6-16-00	1,427	119.7	95.2	155.2	52	16
<b>Total/Avg.*</b>	<b>7,028</b>	<b>124.3</b>	<b>104.7</b>	<b>146.2</b>	<b>52</b>	<b>22</b>

\*Average values for the test run, except for total permeate volume, which is the cumulative volume for the test run.

**Table 4. Summary of Process Measurements**

The target permeate flow rate used by Gates Rubber Company is 1.0 gpm. During operation of the unit, operators periodically check the flow rate. If the flow rate drops below 1.0 gpm, the operator opens the permeate outlet valve until the 1.0 gpm rate is achieved. When such an adjustment is made, a 1 to 3 psi drop in the permeate pressure is observed. During the first test run and the first four days of the second test run, the permeate outlet valve was never in the fully opened position. Only during the fifth day of the second test run was it necessary to fully open the permeate valve in order to maintain a 1.0 gpm permeate flow. Therefore, the unit could have operated at a higher flow rate than 1.0 gpm, except toward the end of the second test run. However, if the unit is operated above 1.0 gpm, the chemical characteristics of the permeate may be different than those measured during verification testing.

## 4.3 Production Data

The alkaline cleaning system connected to the recovery unit tested during this project includes a soak cleaning tank located on the zinc plating line, plus 12 in-process parts washers (see description in section 2.2). The surface area of parts processed through these units during verification testing is summarized in **Table 5**. The number of loads of parts

processed through the soak cleaning tank is shown in column 2. Columns 3 and 4 indicate the percentage of these loads that were transported by barrel or rack. Columns 5 and 6 indicate the surface area of parts processed, respectively, through the soak cleaning tank and small parts washers. Column 7 indicates the total surface area of parts processed in the alkaline cleaning system.

Test Run and Sample Date	Loads/day	Rack %	Barrel %	Soak Cleaning ft <sup>2</sup>	Part Washers ft <sup>2</sup>	Total Area ft <sup>2</sup>
<b>Run 1</b>						
5/22/00	199	0	100	19,900	1,990	21,890
5/23/00	112	0	100	11,200	1,120	12,320
5/24/00	187	0	100	18,700	1,870	20,570
5/25/00	214	0	100	21,400	2,140	23,540
5/26/00	197	0	100	19,700	1,970	21,670
					<b>Total Run 1</b>	<b>114,786</b>
<b>Run 2</b>						
6/12/00	142	33	67	9,795	980	10,775
6/13/00	205	0	100	20,500	2,050	22,550
6/14/00	219	0	100	21,900	2,190	24,090
6/15/00	155	0	100	15,500	1,550	17,050
6/16/00	156	0	100	15,600	1,560	17,160
					<b>Total Run 2</b>	<b>91,625</b>
					<b>Total Runs 1 and 2</b>	<b>206,411</b>

**Table 5. Gates Rubber Company Production (surface area of metal parts cleaned)**

The surface area of parts processed through the soak cleaning was calculated based on the following estimates from Gates Rubber:

- Average surface area of a loaded barrel is 100 ft<sup>2</sup>
- Average surface area of a loaded rack is 6 ft<sup>2</sup>
- Surface area of parts processed through the parts washers is 10% of that processed on the zinc plating line.

The actual surface area of metal parts processed was 114,786 ft<sup>2</sup> during Run 1 and 91,625 ft<sup>2</sup> during Run 2. However, during Run 2, the soil removed from the cleaner during Run 1 was added to the feed solution during Run 2 (see description of test procedures in section 3.2.2). Therefore, the effective surface area processed during Run 2 is the sum of the surface areas from both test runs (206,411 ft<sup>2</sup>).

#### 4.4 Other Data

Other data collected during the course of the verification test are summarized in **Table 6**.

Description	Value
Cost of concentrated alkaline cleaning solution	\$7.48 per gallon
Zinc anode use in 1993*	44,800 lb
Zinc anode use in 1999*	56,700 lb
Alkaline cleaner use in 1993*	8,448 gallons
Alkaline cleaner additions during Test Run #1	19 gallons
Alkaline cleaner additions during Test Run #2	0 gallons
Electricity by cost	0.07 \$/kWh
Natural gas cost	0.35 \$/therm
Labor cost (loaded rate)	\$20.00/hr
Initial cost of Silverback™ Unit	\$36,000 (1999)
Installation cost of Silverback™ Unit	\$7,000 (1999)

\*Data from Gates Rubber historical records

**Table 6. Other Data Collected During Verification**

## 5.0 EVALUATION OF RESULTS

### 5.1 Comparison of Recovered Permeate and Unused 5% Cleaner

There are both similarities and differences between the analytical results of the recovered permeate (EFF) and the calculated results for the 5% cleaner. Total alkalinity is approximately 2 times greater in the recovered permeate than in the fresh 5% solution. The difference in carbonate is even more significant (7.7 times higher in the recovered permeate). The hydroxide concentration of the 5% cleaner is 320 mg/l, while the hydroxide concentrations of the permeate samples were consistently below 1 mg/l. This could be caused by reactions of the solution with atmospheric carbon dioxide, since, as noted in Section 3.2, test runs 1 and 2 were initiated 98 days and 120 days after the cleaning system was recharged with fresh solution. This may account for the fact that the total solids content of the recovered permeate is approximately two times greater than the 5% solution. The increased concentration of total solids is probably due to drag-in from parts, ambient dust, and an accumulation of byproducts from breakdown of organic ingredients of the cleaner. There is very little difference between the recovered permeate and the 5% cleaner with regard to dipropylene glycol ether, a key organic ingredient of the cleaner.

### 5.2 Recovery Efficiency of Alkaline Cleaner Components

Recovery efficiencies were calculated for four dissolved species: total alkalinity, carbonate, bicarbonate, and dipropylene glycol ether. These calculations were performed for each daily set of paired analytical results. The equation for the alkalinity recovery calculation is shown below. The recovery efficiency for other parameters was calculated using a similar equation.

$$A_{\text{eff}} (\%) = [(A_{\text{prod}} \times \text{Prod}_{\text{vol}}) / (A_{\text{feed}} \times \text{Feed}_{\text{vol}})] \times 100\%$$

where:  $A_{\text{eff}}$  = alkalinity recovery efficiency;



$A_{\text{prod}}$  = permeate (EFF) stream alkalinity concentration (grams/liter);  
 $\text{Prod}_{\text{vol}}$  = permeate volume collected during the cycle (liters);  
 $A_{\text{feed}}$  = feed (IN) solution alkalinity concentration (grams/liter); and  
 $\text{Feed}_{\text{vol}}$  = feed solution volume processed during the cycle (liters).

The calculated results for recovery efficiency are shown in **Table 7**.

Test Run and Sample Date	Total Alkalinity % Recovered	Carbonate % Recovered	Bicarbonate % Recovered	Dipropylene Glycol Ether % Recovered
<b>Run 1</b>				
5/22/00	92.6	100.0	98.5	101.6
5/23/00	96.2	92.9	98.5	98.4
5/24/00	100.0	116.7	109.7	96.9
5/25/00	100.0	107.7	101.5	103.3
5/26/00	100.0	100.0	101.5	106.8
<b>Avg. Run 1</b>	97.8	103.5	101.9	101.4
<b>Standard Deviation</b>	3.3	9.1	4.6	3.9
<b>Run 2</b>				
6/12/00	86.4	100.0	85.7	100.0
6/13/00	95.2	100.0	96.2	81.6
6/14/00	100.0	118.2	116.7	100.0
6/15/00	88.0	83.3	86.7	93.3
6/16/00	100.0	94.0	94.0	100.0
<b>Avg. Run 2</b>	93.9	99.1	95.9	95.0
<b>Standard Deviation</b>	6.5	12.7	12.5	8.0

**Table 7. Cleaner Recovery Efficiency**

The average recovery percentages for alkalinity, carbonate, bicarbonate, and dipropylene glycol ether were high (94.0% to 103.2%), indicating that over the short time period of the verification test, there was little or no change in the concentration of these parameters. Recoveries can be greater than 100% due to method error.

### 5.3 Contaminant Removal Efficiency

Contaminant removal efficiencies were calculated for the primary contaminants of the alkaline cleaning bath: oil and TSS. The equation for oil removal efficiency is shown below. The TSS removal efficiency was calculated using a similar equation.

$$O_{\text{eff}} (\%) = 100\% - [((O_{\text{prod}} \times \text{Prod}_{\text{vol}}) / (O_{\text{feed}} \times \text{Feed}_{\text{vol}})) \times 100\%]$$

where:

- $O_{\text{eff}}$  = oil recovery efficiency;
- $O_{\text{prod}}$  = permeate stream oil concentration (grams/liter);
- $\text{Prod}_{\text{vol}}$  = permeate volume collected during the cycle (liters);

$O_{\text{feed}}$  = feed solution oil concentration (grams/liter); and  
 $\text{Feed}_{\text{vol}}$  = feed solution volume processed during the cycle (liters).

The calculated results are shown in **Table 8**.

Test Run and Sample Date	TSS % Removal	Oil % Removal
<b>Run 1</b>		
5/22/00	76.0	81.0
5/23/00	82.4	91.1
5/24/00	73.3	76.3
5/25/00	58.8	91.5
5/26/00	56.2	71.7
<b>Avg. Run 1</b>	<b>69.3</b>	<b>82.3</b>
<b>Std. Dev. Run 1</b>	<b>11.3</b>	<b>8.8</b>
<b>Run 2</b>		
6/12/00	99.8	95.2
6/13/00	97.5	98.3
6/14/00	99.0	97.9
6/15/00	96.7	96.6
6/16/00	79.4	96.8
<b>Avg. Run 2</b>	<b>94.5</b>	<b>97.0</b>
<b>Std. Dev. Run 2</b>	<b>8.5</b>	<b>1.2</b>

**Table 8. Contaminant Removal Efficiency**

During Run 1, the Silverback™ Unit removed an average of 69.3% of the TSS (6.7 lb) and 82.3% of the oil (7.2 lb) from the feed solution, producing a permeate with average concentrations of 52 mg/l TSS and 24.2 mg/l of oil.

During Run 2, the Silverback™ Unit removed an average of 94.5% of the TSS (24.9 lb) and 97.0% of the oil (37.5 lb) from the feed solution, producing a permeate with average concentrations of 13.8 mg/l TSS and 18.4 mg/l of oil.

During Run 1 there was a lower average concentration of TSS in the feed (164.0 mg/l) than during Run 2 (450.0 mg/l). This difference is due to the testing procedure, where adding a concentrated soiled solution to the feed stream intentionally increased the concentration of these contaminants (see section 3.2.2). Despite a higher TSS loading during Run 2, the permeate stream had a lower TSS concentration than in Run 1 (13.8 mg/l vs. 52 mg/l). The average TSS removal efficiency was 69.3% during Run 1 and 94.5% during Run 2. Therefore, the higher removal efficiency during Run 2 was due to the combined effect of a higher average loading concentration and a lower average effluent concentration. The higher efficiency could be due to a higher concentration difference across the membrane.

A similar, but less pronounced pattern, was observed for the oil results. The average oil removal efficiencies were 82.3% for Run 1 and 97.0% for Run 2. The average feed (IN) and permeate (EFF) concentrations during Run 1 were 147.2 mg/l and 24.2 mg/l, respectively. During Run 2, the average feed and permeate concentrations were 660 mg/l and 18.4 mg/l, respectively.

#### 5.4 Mass Balance

Mass balance calculations were performed to evaluate how effectively the sampling and analytical procedures account for certain key parameters. The equation for mass balance uses the equation for recovery efficiency (section 5.3) and adds a term for the quantity of material contained in the recovery tank at the end of the test run (R-1 and R-2). A calculated result of 100% indicates that the quantity of a particular parameter found in the feed stream (IN) is fully accounted for in the permeate (EFF) and recovery tank (R). Mass balance values were calculated for the following parameters: total alkalinity, TSS, total solids, oil, and dipropylene glycol ether. The mass balance equation for alkalinity is shown below. The mass balance for the other constituents was calculated using the same equation.

$$\text{mass bal. (\%)} = [(A_{\text{prod}} \times \text{Prod}_{\text{vol}}) + (A_{\text{waste}} \times \text{Waste}_{\text{vol}})] / (A_{\text{feed}} \times \text{Feed}_{\text{vol}}) \times 100\%$$

where:  $A_{\text{waste}}$  = waste stream (R) alkalinity concentration (grams/liter); and  
 $\text{Waste}_{\text{vol}}$  = waste stream volume (liters).

The mass balance results are shown in **Table 9**.

Test Run	Oil %	TSS %	Total Solids %	Total Alkalinity %	Dipropylene Glycol Ether %
Run 1	64.2	117.4	95.6	99.5	102.9
Run 2	37.3	24.3	108.2	96.4	96.2

**Table 9. Mass Balance Results**

The mass balance results for total solids, total alkalinity and dipropylene glycol ether are close to 100%, indicating that quantities of these parameters found in the feed stream (IN) are accounted for in the permeate (EFF) and recovery tank (R) samples. The results for oil and TSS are variable. The TSS value during Run 1 was high (117.4%), but within a reasonable percentage error of +/- 25. The low percentage results for oil (Runs 1 and 2) and TSS (Run 2) may be due to the difficulty of collecting a representative sample from the recirculation tank (R). These samples were grab samples collected at the end of each run. Although the recirculation pump was operating at the time of sampling, complete mixing may not have been achieved. The bottom of the recirculation tank is sloped, and it is suspected that a layer of sludge containing solids and possibly entrained oil accumulated on this sloped surface, and was not within the recirculated solution that was sampled. This

situation would have been accentuated during Run 2, where the TSS and oil loading were significantly higher than Run 1. The parameters for which the mass balance percentages were close to 100% were dissolved species and, therefore, would be less affected by the presence of a sludge layer. Recoveries higher than 100% are due to inherent method error.

## 5.5 Energy Use

The primary energy requirements for operating the Silverback™ Unit at Gates Rubber Company include electricity for the system pump and steam (from a natural gas fired boiler) for reheating the permeate solution when it is returned to service. Electricity is also used for instrumentation and compressed air, however, the energy requirements for these are less significant and were not evaluated during this project.

Electricity use was calculated by dividing the horsepower (HP) of the system pump (7.5 HP) by 1.341 HP-hr/kWh. The result is 134.3 kWh/day, based on continuous use of the pump.

The energy required to raise the solution temperature of the permeate solution was calculated using the following equation:

$$(\text{BTUs/cycle}) = \text{Prod}_{\text{vol}} \times 2.2 \frac{\text{lb}}{\text{L}} \times \Delta T \times 1 \frac{\text{BTU}}{\text{lb}^\circ\text{F}}$$

where:  $\text{Prod}_{\text{vol}}$  = permeate volume collected during the cycle (liters); and  
 $\Delta T$  = average temperature difference between recovered permeate tank and soak cleaning tank (°F).

The average volume of solution processed per day during the test period was 1,415 gal./day (5,356 liters/day). The average temperature of the permeate was 121.2°F and the average temperature of the soak cleaning tank was 144.1°F. Using the above equation, the resultant energy requirement is 271,000 BTUs/day. The amount of natural gas required to generate this quantity of energy is approximately 2.7 therms/day (based on 100,000 BTU/therm).

## 5.6 Operations and Maintenance Labor Analysis

Operations and maintenance (O&M) labor requirements for the recycling system were observed during testing. Prior to each test run, the unit was drained and cleaned (see Section 2.3). This process took two labor hours<sup>6</sup> to complete and it was performed once each week. On a daily basis, operators periodically checked the permeate flow rate and made adjustments, if necessary. Also, on a daily basis, the operator removed the cover of the unit and observed the feed going into the bag filter. If the solution was overflowing the bag filter, instead of passing through it, the operator removed the bag filter, cleaned it, and returned it to the unit. These daily tasks took approximately 1.75 hr each week (i.e., 15 minutes per day) to perform. Therefore, the total O&M labor associated with the unit at

<sup>6</sup> The task took 3.0 hours to complete. However, during certain steps, operator labor was not necessary and the operator was free to perform other tasks; the actual labor hours applied to the Silverback™ unit were estimated to be 2.0 hours.

Gates Rubber Company is 3.75 hr/wk. (50 wk/yr, 187.5 hr/yr). No additional O&M tasks were performed during the test period.

Other operation and maintenance labor associated with the alkaline cleaning system, which is affected by the installation of the recycling unit, is associated with the disposal and make up of bath chemistries. This process involves draining the alkaline cleaning tank, cleaning it, and refilling it with fresh chemicals. This process takes eight hours to complete. Prior to the installation of the recovery unit, the alkaline cleaning tank was drained and filled 15 times per year (120 hr/yr). After the recovery unit was installed, the frequency was reduced to twice per year (16 hr/yr).

### 5.7 Chemical Use Analysis

Prior to the installation of an alkaline cleaner recovery unit, Gates Rubber Company used 8,448 gal/yr of their concentrated cleaner, CLEAN-R-120GR (data from 1993).<sup>7</sup> Adjusted for changes to production volume, an equivalent quantity for 1999 is 10,729 gal/yr.<sup>8</sup> During 1999, Gates Rubber Company actually used 5,390 gal/yr of the concentrated cleaner product. Therefore, the production-adjusted savings in cleaner use is 5,339 gal/yr (10,729 gal/yr - 5,390 gal/yr).

With the present operating practices at Gates Rubber Company, concentrated cleaner is used when formulating the alkaline cleaning bath two times per year, and it is added as needed to maintain the alkalinity of the alkaline cleaning bath, as discussed in Section 2.2. Alkaline constituents are consumed during the cleaning process, and are also lost from the bath due to drag-out. Concentrated cleaner is also used during the Silverback™ Unit cleaning cycle described in Section 2.3. The approximate volumes of cleaner used for these three purposes at Gates Rubber Company in 1999 were:

- Formulating fresh bath: 360 gal/year
- Added as makeup to maintain alkalinity: 4,822 gal/year
- Used to clean the Silverback™ Unit: 208 gal/year
- Total use in 1999: 5,390 gal.

CLEAN-R-120GR, peroxide, and hydrochloric acid are used to clean the Silverback™ Unit and filter module (see description of cleaning process in section 2.3). The annual quantities of these chemicals used in 1999 were:

- CLEAN-R-120GR: 200 gal/yr
- Peroxide: 12.5 gal/yr

<sup>7</sup> In 1994 Gates Rubber Company implemented a polymer membrane, alkaline cleaner recovery unit and subsequently replaced that equipment with the Silverback™ unit. Therefore, 1993 is the most recent year that is representative of using the alkaline cleaning system without a recovery unit installed.

<sup>8</sup> This adjustment was calculated using zinc anode purchases as a normalizing factor. Zinc anodes are used on the zinc plating line and are a good indicator of overall production volume at this site. Zinc anode purchases in 1993 and 1999 were 44,800 lb/yr and 56,700 lb/yr, respectively. Therefore, under the same conditions, if Gates Rubber Company used 8,448 gal of cleaner in 1993, they would be expected to use 10,729 gal in 1999.

- Hydrochloric acid: 200 gal/yr.

## 5.8 Waste Generation Analysis

Prior to the installation of the recovery unit, the alkaline cleaning bath was drained and fresh chemistry was added 15 times per year. During use, the alkaline cleaning system generated a discharge from the rinse tank following the alkaline cleaning tank. This discharge from rinsing was estimated to be 1 gpm. The used rinse water was treated on-site. This information could not be verified during the project. The treatment process generated a sludge that was sent off-site for disposal. The quantity of sludge generated prior to the Silverback™ installation could not be quantified during this project. Overall, the bath replacement procedure generated the following wastes:

- Spent alkaline cleaning solution
- Dilute wastewater from tank washdown
- Rinsewater following alkaline cleaning step (dilute wastewater)
- Wastewater treatment sludge.

Waste oil is generated by skimming oil off of waste storage tanks in the waste treatment area. Waste oil was generated in similar quantities before and after the installation of the Silverback™ Unit. Gates sends about 500 gallons of waste oil offsite every two years. The cost of hauling/disposal is \$1.00/gal. There is no waste reduction or cost savings that have resulted by installation of the Silverback™ Unit, with respect to waste oil.

Following installation of the recovery unit, the alkaline cleaning system is drained and replaced two times each year. The recovery unit is drained and cleaned weekly. This procedure generates a concentrated waste and dilute wastewater (from cleaning the unit's tank and filter module). These liquid wastes are combined with other wastewaters and treated on-site. The quantity of sludge generated could not be quantified during this project. Overall, this procedure generated the following wastes<sup>4</sup>:

- Spent alkaline cleaning solution
- Wastewater from tank washdown (dilute wastewater)
- Weekly draining of recovery unit
- Weekly cleanout of recovery unit (dilute wastewater)
- Wastewater treatment sludge

The results of the waste generation analysis (concentrated wastes only) are shown in **Table 10**.

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<sup>4</sup> The Silverback™ Unit has a drain port located on the upper part of the settling tank that can be used to remove floating oil from that tank (see description in Section 2.1). This drain is not used at Gates Rubber Company and therefore a separate oil waste is not generated during the recovery process.

Waste Type	Waste Volume gal/yr	Total Solids lb/yr <sup>5</sup>
<b>Without Silverback™ Unit</b>		
Spent alkaline cleaning solution	37,500	3,039
<b>Totals without Silverback™ Unit</b>	37,500	3,039
<b>With Silverback™ Unit</b>		
Spent alkaline cleaning solution	7,200	583
Weekly draining of recovery unit	5,000	665
<b>Totals with Silverback™ Unit</b>	12,200	1,248

**Table 10. Results of Waste Generation Analysis**

The quantity of sludge generated from treatment of the liquid wastes could not be quantified during this project because liquid wastes from various sources are combined prior to treatment at Gates Rubber Company. However, the quantity of sludge generated with and without the recovery unit is expected to be in proportion to the total solids content of the wastes generated.

**5.9 Cost Analysis**

The capital cost of the Silverback™ Unit was \$43,000 (1999; includes \$36,000 for the unit, \$5,000 for storage tanks and plumbing, and \$2,000 for installation costs).

Annual costs and savings associated with the alkaline cleaner recovery operation are shown in **Table 11**. The operating costs of the Silverback™ Unit are \$50,049. The operating costs prior to installation of the Silverback™ Unit were \$82,653, resulting in a net annual savings of \$32,604. The simple payback period is 1.3 years (capital cost/net annual savings).

Waste treatment and sludge disposal costs could not be quantified and are not included in the above analysis.



Item	Prior to Installation of Silverback™			After Installation of Silverback™		
	Units	Unit Cost \$/unit	Cost \$	Units	Unit Cost \$/unit	Cost \$
Recycling unit O&M labor (see section 5.6)	0	N/A	0	187.5 hr	20.00	3,750
Alkaline Clean tank maintenance O&M labor (see section 5.6)	120 hr	20.00	2,400	16 hr	20	320
Alkaline cleaner (see section 5.7)	10,729 gal	7.48	80,253	5,390 gal	7.48	40,317
Tank/module cleaning chemicals (see section 5.7)	0	N/A	0	50	40.92	2,046
Electricity for recovery unit (see section 5.5)	0	-	0	47,005 kWh	0.07	3,290
Natural gas for recovery process (see section 5.5)	0	-	0	941.5 therms	0.35	326
<b>Total Costs</b>			<b>82,653</b>			<b>50,049</b>

**Table 11. Annual Costs/Savings**

### 5.10 Project Responsibilities/Audits

No audits were performed during the course of this project. Verification testing activities and sample analysis were performed according to Section 5.0 of the Verification Test Plan (Ref 1).

### 6.0 REFERENCES

All references are available by accessing the ETV-MF Program Internet website at: [www.etv-mf.org](http://www.etv-mf.org).

1. Concurrent Technologies Corporation, *“Environmental Technology Verification Program for Metal Finishing Pollution Prevention Technologies Verification Test Plan, Evaluation of USFilter Membralox® Silverback™ Model 900 Alkaline Cleaner Recycling System.”* April 4, 2000.

2. Concurrent Technologies Corporation, *“Environmental Technology Verification Program Metal Finishing Technologies Quality Management Plan.”* December 9, 1998.



## **APPENDIX A**

### **PRECISION CALCULATIONS**

## PRECISION CALCULATIONS

Amtest ID	CTC ID	Parameter	Units	Sample Value	Duplicate Value	RPD %	RPD % Limits	RPD Met Y/N
8091	IN-3	alkalinity	mg/l	2,600	2,600	0	< 30	Y
8091	IN-3	carbonate alkalinity	mg/l	1,200	1,300	8.0	< 30	Y
8091	IN-3	bicarbonate alkalinity	mg/l	620	640	3.2	< 30	Y
8091	IN-3	hydroxide alkalinity	mg/l	< 1	< 1	0	< 30	Y
7756	EFF-2	ammonia nitrogen	mg/l	4.1	4.6	11.0	< 30	Y
7753	IN-1	ammonia nitrogen	mg/l	2.8	3.0	6.9	< 30	Y
8091	IN-3	total nitrogen	mg/l	3.0	3.6	18	< 30	Y
8099	R-1	TSS	mg/l	10,000	10,000	0	< 30	Y
8095	EFF-4	TSS	mg/l	66.0	66.0	0	< 30	Y
8091	IN-3	total solids	mg/l	9,600	9,600	0	< 30	Y
8091	IN-3	phosphate (as P)	mg/l	389	393	1.0	< 30	Y
7754	EFF-1	alkalinity	mg/l	2,500	2,600	3.9	< 30	Y
7754	EFF-1	carbonate alkalinity	mg/l	1,300	1,300	0	< 30	Y
7754	EFF-1	bicarbonate alkalinity	mg/l	640	660	3.1	< 30	Y
7754	EFF-1	hydroxide alkalinity	mg/l	< 1	< 1	0	< 30	Y
7753	IN-1	ammonia nitrogen	mg/l	2.8	3.0	6.9	< 30	Y
8094	IN-4	ammonia nitrogen	mg/l	1.1	1.2	8.7	< 30	Y
7753	IN-1	total nitrogen	mg/l	2.8	2.5	11.0	< 30	Y
7753	IN-1	total phenol	mg/l	0.59	0.58	1.7	< 30	Y
7756	EFF-2	TSS	mg/l	30.0	28.0	6.9	< 30	Y
7753	IN-1	total solids	mg/l	9,600	9,500	1.0	< 30	Y
7755	IN-2	oil	mg/l	180	140	25.0	<30	Y
7753	IN-1	phosphate (as P)	mg/l	397	398	0.25	< 30	Y
9071	IN-6	alkalinity	mg/l	2,200	2,200	0	< 30	Y
9071	IN-6	carbonate alkalinity	mg/l	1,000	1,000	0	< 30	Y
9071	IN-6	bicarbonate alkalinity	mg/l	560	560	0	< 30	Y
9075	IN-7A	oil	mg/l	750	720	4.1	<30	Y
9233	IN-8	ammonia nitrogen	mg/l	1.4	1.4	0	< 30	Y
9076	Clean-1	total nitrogen	mg/l	< 0.25	< 0.25	0	< 30	Y
9073	IN-7	phosphate (as P)	mg/l	490	503	2.6	< 30	Y
9233	IN-8	ammonia nitrogen	mg/l	1.4	1.4	0	< 30	Y
9236	EFF-9	oil	mg/l	18	18	0.1	<30	Y
9236	EFF-9	total solids	mg/l	8,300	8,200	1.2	< 30	Y
9233	IN-8	phosphate (as P)	mg/l	418	429	2.6	< 30	Y
9076	Clean-1	total nitrogen	mg/l	< 0.25	< 0.25	0	< 30	Y
9433	IN-10	total phenol	mg/l	0.47	0.51	8.2	< 30	Y
9436	Dirty-10A	total solids	mg/l	88,000	85,000	3.5	< 30	Y
9433	IN-10	phosphate (as P)	mg/l	322	358	11.0	< 30	Y

## **APPENDIX B**

### **ACCURACY CALCULATIONS**

## ACCURACY CALCULATIONS

SAMPLE ID	Parameter	Units	Sample Value	Sample +Spike Value	Spike Value	Recovery %	Target % Recovery	Accuracy Met? Y/N
EFF-2	ammonia nitrogen	mg/l	4.1	10	5	118	80-120	Y
EFF-1	ammonia nitrogen	mg/l	3.7	8.3	5	92	80-120	Y
EFF-4	ammonia nitrogen	mg/l	3.3	8.2	5	98	80-120	Y
EFF-3	total nitrogen	mg/l	23.0	130	100	107	80-120	Y
EFF-1	total phenol	mg/l	0.57	2.5	2	96	80-120	Y
EFF-3	phosphate (as P)	mg/l	393	482	90	98.9	80-120	Y
EFF-6	phosphate (as P)	mg/l	318	400	90	91.1	80-120	Y
EFF-8	phosphate (as P)	mg/l	357	440	90	92.2	80-120	Y
EFF-1	ammonia nitrogen	mg/l	3.7	8.3	5	92.0	80-120	Y
EFF-1	total nitrogen	mg/l	3.8	14.0	10.0	102	80-120	Y
IN-7	ammonia nitrogen	mg/l	1.9	7.2	5.0	106	80-120	Y
Clean-1	total nitrogen	mg/l	< 0.25	1.1	1.0	110	80-120	Y
EFF-1	total phenol	mg/l	0.57	2.5	2	96.5	80-120	Y

Accuracy for the oil determinations could not be determined by the addition of spikes to analysis samples because the spike would be obscured by the magnitude of the sample. Accuracy for the oil analyses was determined by duplicate analyses of spikes added to a blank matrix from which percent recoveries were calculated. A blank matrix spiked with 4088 µg of oil was analyzed with results of 2560 µg/l and 2440 µg/l to yield recoveries of 62 and 59 percent, respectively. A second accuracy check of a matrix spiked with 2307.2 µg/l of oil had results of 2640 µg/l and 1680 µg/l for recoveries of 114% and 73%.

A check standard containing 300 µg/l was analyzed and yielded results of 260, 330, 282, and 293 µg/l for recoveries of 86, 110, 94, and 98 percent.

All accuracy checks for oil were within the goal of 50-150%.



## APPENDIX C

### REPRESENTATIVENESS CALCULATIONS



REPRESENTATIVENESS CALCULATIONS

Sample	Total Alkalinity mg/l as CaCO <sub>3</sub>	Carbonate mg/l as CaCO <sub>3</sub>	Bicarbonate mg/l as CaCO <sub>3</sub>	Hydroxide mg/l as CaCO <sub>3</sub>	Dipropylene Glycol Ether mg/l	Ammonia Nitrogen mg/l	Total Nitrogen (TKN) mg/l	Total Phenol mg/l	Total Suspended Solids mg/l	Total Solids mg/l	Phosphate (as P) mg/l	Oil mg/l
EFF-3	2,600	1,400	680	< 1	6,200	3.5	23	0.42	48	9,200	390	18
EFF-3A	2,600	1,300	640	< 1	6,300	2.5	24	0.43	56	9,300	400	16
% Difference	0.0	7.4	6.1	0.0	-1.6	33.3	-4.3	-2.4	-15.4	-1.1	-2.6	11.8
IN-7	2,100	1,100	520	< 1	5,700	1.9	43	0.7	910	11,000	490	1,000
IN-7A	2,500	1,200	600	< 1	4,800	1.6	40	0.59	850	9,500	430	750
% Difference	-17.4	-8.7	-14.3	0.0	17.1	17.1	7.2	17.1	6.8	14.6	13.0	28.6
R-2	3,900	1,000	520	< 1	5,200	3.4	44	0.95	6,700	85,000	990	16,000
R-2A	2,500	990	500	< 1	5,000	3.9	35	0.93	8,000	88,000	1,000	16,000
% Difference	43.8	1.0	3.8	0.0	3.8	-13.7	22.8	2.1	-17.7	-3.5	-1.0	0.0



**APPENDIX D**

**OIL ANALYSIS**

**EPA METHOD 8015 (MODIFIED)**

**(NORTHWEST TOTAL PETROLEUM HYDROCARBON –  
EXTENDED DIESEL (NWTPH-DX))**

## NWTPH-DX Diesel Range Organics In Soil And Water

### Summary

The NWTPH-D Method adapts EPA SW-846 Methods 3540 and 8000 and covers the quantitative analysis of semi-volatile petroleum products in soils. The method involves extracting the sample with methylene chloride and injecting of a portion of the extract into a gas chromatograph equipped with a flame ionization detector. This method specifies criteria for the identification and quantitation of semi-volatile petroleum products. When the type of fuel is unknown #2 diesel is used to quantitate the sample. The reporting limit is 25 mg/kg for soil and 0.10 mg/l for water samples eluting from the jet fuels range to the diesel #2 range. For petroleum products eluting after diesel #2, the reporting limits are 100 mg/kg for soil and 0.20 mg/l for water (assuming 100 % total solids for soil).

### Equipment and Reagents

The following equipment and reagents are required:

Gas Chromatograph

Flame Ionization detector

Column: J & W DB-5 30M x .32mm with 0.25um film thickness  
Capillary column

Maxima Data System

Analytical Balance accurate to at least 0.001g

Horn Sonicator

Volumetric Flasks, 10ml Ground Glass Stopped

150 ml beakers

Sodium Sulfate

Methylene Chloride

K-D Equipment (refer to K-D section)

Nitrogen evaporator

Sulfuric Acid, concentrated

Silica Gel cartridges

Various Petroleum products for standards.

### Collection Requirements

All samples should be collected in I-Chem containers and preserved at 4 degrees Celsius until extracted. The holding time from the date of collection to extraction, is 14 days for soils and preserved water. For unpreserved water, the holding time is seven days. Preservation is accomplished by adjusting pH to about 2 using an 1:1 HCl aqueous solution.

## Standards

### Fuel Stock Standard

Choose the appropriate fuel for comparison to the sample fingerprint. Weigh approximately 0.10 g into a 10-ml volumetric flask and dilute to volume with DCM. Label and record the exact concentration.

Calculate the concentration as follows:

$$\text{Stock Conc. } (\mu\text{g/ml}) = \frac{\text{weight diesel (g)} \times 1,000,000 (\mu\text{g/g})}{10 \text{ ml}}$$

### Calibration Standard

Prepare calibration standards from the stock diesel standard at concentrations of 25, 50, 200, and 300  $\mu\text{g/ml}$  by adding appropriate volumes to a 10-ml volumetric flask and diluting to volume with methylene chloride. For fuels heavier than diesel #2, prepare standards at concentrations of 50, 100, 150, 300, and 400  $\mu\text{g/ml}$ .

To calculate volume (ul) of stock standard to add to 10-ml vol. flask use the equation below:

$$\text{Volume Diesel Stock (ul)} = \frac{\text{Cal. Std. Conc. } \mu\text{g/ml} \times 1000 \mu\text{g} \times 10}{\text{Diesel Stock } \mu\text{g/ml}}$$

Dilute the flask to 10 ml with DCM.

### Stock Surrogate Standard

Make up a surrogate of bromofluorobenzene and 2-fluorobiphenyl, which contains approximately 8,000  $\mu\text{g/ml}$  by weighing about 0.080 g of the surrogate compounds into a 10-ml volumetric flask and filling to volume with methylene chloride.

### Working Surrogate Spike (800 $\mu\text{g/ml}$ )

Add the appropriate volume of the stock standard to a 10-ml volumetric flask, which has been filled with 5 ml of methylene chloride, taking care not to add the surrogate standard solution into the solvent without contacting the neck of the flask. Fill the flask to volume, stopper and mix. Store at 4 °C.

$$\text{Volume Surrogate Stock } (\mu\text{l}) = \frac{800 \mu\text{g/ml} \times 10 \text{ ml} \times 1,000 \mu\text{l}}{\text{Surrogate Stock Conc. } \mu\text{g/ml}}$$

### GC/FID PARAMETERS FOR FUEL SCANS

#### Instrument Parameters:

Column:	J & W DB-5 30M x .32mm with 0.25 um film thickness, capillary column
Injection Sample Volume:	2 ul
Injector Temperature:	290 °C
Ion Block Temperature:	300 °C
Initial Temperature:	35 °C
Initial Time:	5 minutes
Initial Rate:	10 degrees/min
Final Temperature:	300 °C
Final Time:	5 minutes
Purge Valve On Time:	1.5 minutes
Purge Valve Off Time:	36 minutes
Purge Valve On Time:	1.5 minutes
Purge Valve Off Time:	36 minutes
Hydrogen Flow:	25 – 30 ml/min
Air Flow:	300 – 400 ml/min
Make-up Gas Flow:	30 ml/min
Carrier Gas:	Helium
Helium Carrier gas Head Pressure:	12 psi

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#### Sample Extraction Soil

Accurately weigh approximately 20 grams of soil (note that if the sample is hydrated, more than 20 grams are needed) and 20 grams of anhydrous sodium sulfate and place into a 150-ml beaker and mix completely with a spatula. The mixture should have a grainy texture. If it forms a clump, add more sodium sulfate, grind to a grainy texture and note this in the extraction log. Add 100 ul of Working Surrogate spike and 50 ml of methylene chloride; sonicate this for 3 minutes utilizing the horn sonicator. (Refer to Horn sonicator instructions at the end of this SOP if unfamiliar with the operation of the instrument).

Allow the mixture to stand. Collect the extract in a 250 ml Kuderna-Danish (K-D) Flask to which is connected a 10- ml concentrator tube and a sodium sulfate drying apparatus.

Repeat the extraction twice more using 50ml of methylene chloride and add the extract to the same K-D flask. Attach a 3-ball Snyder column and concentrate the extract to a final volume of 10 ml. If the extract is highly colored or forms a precipitate, a dilution may be necessary to stay within the calibration range. If samples need to be cleaned up, refer to "Clean-up" procedure at the end of this method.

Store the samples at 4 °C in a glass vial until ready for analysis.

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### **Water Extraction Procedure**

Pour 500 ml of the sample into a 2-liter separatory funnel. Adjust the pH to 2 if needed. Add 200 ul of surrogate working standard. Extract the sample with 50 ml of DCM. Pour the extract through sodium sulfate into a K-D set up. Extract the sample twice more with 50 ml DCM, adding the extract to the K-D set up. Concentrate the sample to 5 – 10 ml on a steam bath. Remove the ampule and continue to concentrate on a N-Vap to below 2 ml. Adjust the final volume to 2 ml in a volumetric flask. Clean-up the sample if needed using the procedure at the end of the SOP.

Determine the Total Solids Percentage of soil sample.

### **GC Run to include the following:**

1. Five point calibration curve
2. 10 % duplicates
3. Surrogate std (100 µg/l working surrogate spike to 10 ml)
4. Mid standard check every ten samples analyzed
5. End standard check at the end of each run.

### **Data Validation:**

1. Continuing calibration checks and end checks must fall +/- 15 % of the known value of the standard
2. Surrogate recoveries must be between 50 % - 150 %
3. Standard curve must have a minimum correlation of 0.99.

### **Sample Calculations**

The retention time range windows for integration must be adjusted to incorporate the majority of the components of the petroleum product of interest. If an exact match cannot be made, a standard is chosen that closely represents the sample. In all cases, the selected retention time window used for quantitation must, at a minimum, include any unresolved envelope of compounds as well as all discrete components peaks with an area greater than or equal to 10% of the largest peak. These must be integrated to the baseline as a group.

Be sure to subtract the area of the surrogates if the surrogate falls within the retention time window.

Adjustments of retention time windows may be made if interferences are present, i.e, overlap of oil into diesel area.

$$\text{Sample Conc. (mg/kg)} = \frac{\text{Sample conc. } \mu\text{g/ml} \times V \times \text{DF}}{\text{Sample weight} \times \text{TS}}$$

where: V = Final Volume of extract  
DF = Dilution Factor  
TS = Decimal percent solids of sample.

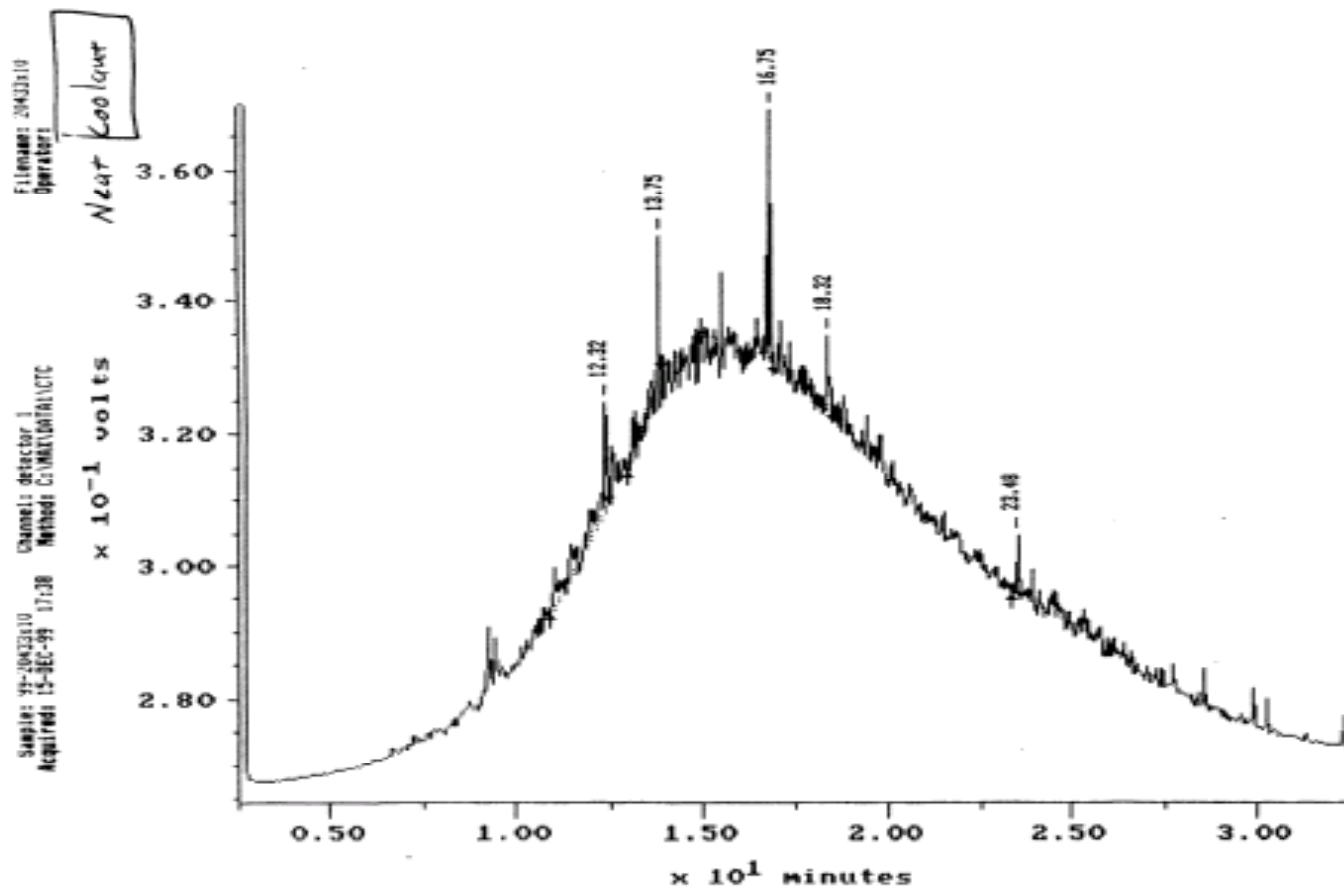
### **Horn Sonicator Settings**

Sonicator Type: Ultrasonic, Inc. Model W-385 (475 watt) with No. 207, ¾-inch Tapped Disruptor Horn  
Settings: 3 minutes  
Output Control Knob: 10  
Mode: Pulse  
Percent Duty Knob: 50 %.

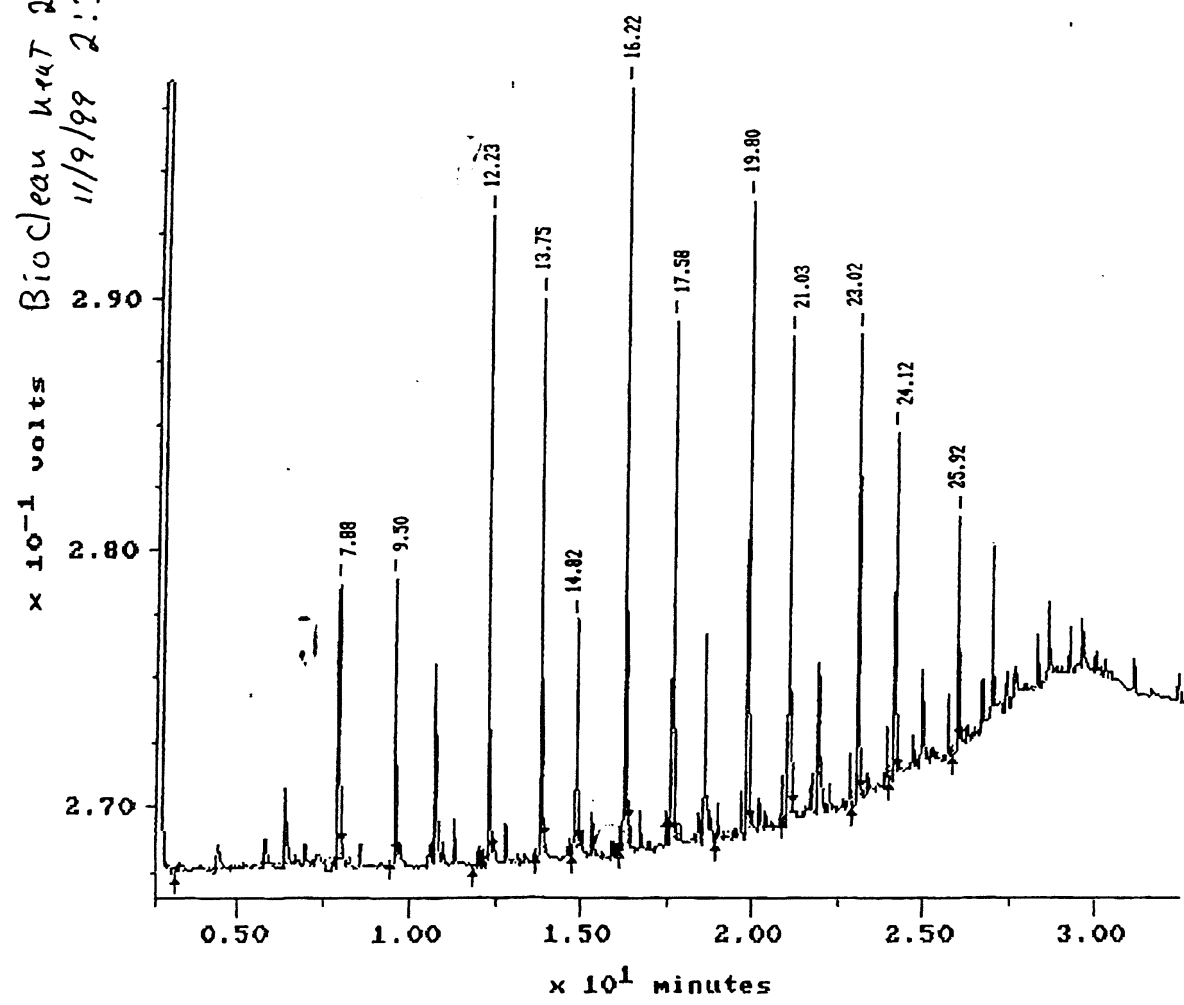
### **Sample Clean-up Procedure**

When samples contain a significant amount of naturally occurring non-petroleum organics, e.g. leaf litter, bark, etc. which may contribute to biogenic interference, the following clean-up technique may be employed to assist in their reduction or elimination.

1. Transfer 2 ml of the sample extract to a 4-ml vial
2. Add 0.3 to 0.5 ml concentrated sulfuric acid to the vial and shake for one minute
3. Allow the phases to separate and transfer the upper layer to another 4-ml vial
4. Add about .4 g of silica to the vial and shake
5. Repeat the procedure a second time: transfer the cleaned extract to an auto sampler vial for analysis
6. If the clean-up affects the analyte of interest, clean the standards in the same way as the samples.



BioClean MET 20/100  
11/9/99 2:30 PM





**APPENDIX E**

**DIPROPYLENE GLYCOL ETHER ANALYSIS**

**AMTEST**  
**LABORATORIES**

December 15, 2000

Concurrent Technology  
Marion Rideout

Re: Glycol Analysis

At AMTest, we analyze glycol by GC/FIU. The method is one provided by Texaco 10 years ago, which they developed. We have been routinely using this method since then. The method uses a GC with FID detector and a DB wax column. Each sample was diluted with reagent alcohol (0.50 ml sample to 4.50 ml alcohol) and injected directly onto the column. The standard was provided by your client.

**ANALYSIS OF GLYCOLS FOR CTC**

**I) Sample preparation**

- 1). Dilute 0.5 ml of sample to 5 mls final volume with reagent alcohol.
- 2). Filter sample if needed to remove solid material through a 0.45 urn teflon filter.
- 3). Transfer approximately 2mLs to a GC vial for analysis

**II) GC/Analysis**

- 1). GC Parameters

DB Wax Column 30 m O.53 um I.D. 1 um Film thickness

Detector Temperature 250 C

Injector Temperature 200 C

Initial Temperature 30 C

Intitial Time 5.00 min.

Rate 5 C/min.

Final Temperature 200

Final Time 0 min.

- 2). Prepare 5 point standard curve covering the range of 5 ppm to 100 ppm.
- 3). Inject 2 ul of standards and samples.
- 4). Quantitate results based on the linear curve established
- 5). Sample exceeding the standard curve must be diluted and re-analyzed.