



## **ENVIRONMENTAL SECURITY TECHNOLOGY CERTIFICATION PROGRAM**

### **SODIUM HYDROXIDE RECYCLING AND RECOVERY AT WATERVLIET ARSENAL**



**Final Report  
October 15, 2002**

# Report Documentation Page

*Form Approved*  
*OMB No. 0704-0188*

Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.

1. REPORT DATE <b>15 OCT 2002</b>	2. REPORT TYPE	3. DATES COVERED <b>00-00-2002 to 00-00-2002</b>			
4. TITLE AND SUBTITLE <b>Sodium Hydroxide Recycling and Recovery at Watervliet Arsenal</b>		5a. CONTRACT NUMBER			
		5b. GRANT NUMBER			
		5c. PROGRAM ELEMENT NUMBER			
6. AUTHOR(S)		5d. PROJECT NUMBER			
		5e. TASK NUMBER			
		5f. WORK UNIT NUMBER			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) <b>U.S. Army Benet Laboratories, 1 Buffington Street, Watervliet, NY, 12189-4000</b>		8. PERFORMING ORGANIZATION REPORT NUMBER			
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)		10. SPONSOR/MONITOR'S ACRONYM(S)			
		11. SPONSOR/MONITOR'S REPORT NUMBER(S)			
12. DISTRIBUTION/AVAILABILITY STATEMENT <b>Approved for public release; distribution unlimited</b>					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT <b>unclassified</b>	b. ABSTRACT <b>unclassified</b>	c. THIS PAGE <b>unclassified</b>	<b>Same as Report (SAR)</b>	<b>44</b>	

# SODIUM HYDROXIDE RECYCLING AND RECOVERY AT WATERVLIET ARSENAL

## Table of Contents

TABLE OF CONTENTS .....	i
ACKNOWLEDGEMENTS .....	iii
1. INTRODUCTION.....	1
1.1 Background Information .....	1
1.2 Official DOD Requirement .....	1
1.3 Objectives of the Demonstration.....	2
1.4 Regulatory Issues.....	2
1.5 Previous Testing of the Technology.....	3
2. TECHNOLOGY DESCRIPTION .....	4
2.1 Description.....	5
2.2 Strengths, Advantages and Weaknesses .....	7
2.3 Factors Influencing Cost and Performance .....	7
2.4 Technical Overview .....	8
3. SITE FACILITY DESCRIPTION .....	11
3.1 Background.....	11
3.2 Site/Facility Characteristics .....	11
3.2.1 Watervliet Arsenal Description.....	11
3.2.2 Corpus Christi Army Depot Description.....	12
4. DEMONSTRATION APPROACH.....	13
4.1 Performance Objectives .....	13
4.2 Demonstration Setup, Commencement and Operation .....	13
4.3 Sampling Procedure .....	15
4.4 Analytical Procedures .....	17
5. PERFORMANCE ASSESSMENT.....	18
5.1 Performance Data .....	18
5.2 Data Assessment.....	19
5.3 Technology Comparison .....	20
6. COST ASSESSMENT .....	30
6.1 Cost Performance.....	30
6.2 Cost Comparison to Conventional and other Technologies .....	30
7. REGULATORY ISSUES .....	31
7.1 Approach to Regulatory Compliance and Acceptance.....	31
8. TECHNOLOGY IMPLEMENTATION .....	31
8.1 DOD Needs.....	31
8.2 Transition .....	31

# SODIUM HYDROXIDE RECYCLING AND RECOVERY AT WATERVLIET ARSENAL

## Table of Contents (Cont'd)

9. LESSONS LEARNED .....	31
10. FINAL COMMENTS, RECOMMENDATIONS, and CONCLUSIONS	
for Caustic and Solvent Recycling using Vibratory Shear Enhanced Processing (V $\phi$ SEP).....	33
10.1 Concentrate Valve Control Issues:.....	33
10.2 System Startup Instability Issues:.....	34
10.3 General System Instability Issues:.....	35
10.4 RECOMMENDATIONS .....	36
10.5 CONCLUSIONS .....	39
11. REFERENCES .....	40
APPENDIX A - Points of Contacts	
APPENDIX B - Operations Manual and System Components for V $\phi$ SEP Unit .....	
APPENDIX C - Health and Safety .....	
APPENDIX D - List of Acronyms .....	
APPENDIX E – Final Report Corpus Christi Army Depot .....	
APPENDIX F - Testing and Evaluation Plan for Watervliet Arsenal.....	
APPENDIX G - Membrane Selection Process.....	
APPENDIX H – CCAD Final Report .....	
<b>List of Figures and Tables</b>	
Figure 2.1 V $\phi$ SEP Unit .....	5
Figure 2.2 Process Flow Diagram.....	6
Figure 2.3 Cross Flow vs. V $\phi$ SEP .....	10
Figure 3.1 NYS Map Watervliet Location .....	11
Figure 5.1 Five Feed Samples Picture .....	21
Figure 5.2 Two Feed Samples Picture .....	22
Figure 5.3 Three Samples Picture .....	23
Figure 5.4 IR Spectra- Control Sample .....	26
Figure 5.5 IR Spectra- Feed Sample .....	27
Figure 5.6 IR Spectra- Permeate Sample .....	28
Figure 5.7 IR Spectra- Concentrate Sample .....	29
Table 4.2 Analytical Methods.....	17
Table 5.1 Analytical Data.....	24
Table 5.2 Analytical Data - continued .....	25

## **Acknowledgements**

Benet Laboratories –TACOM ARDEC, Watervliet, New York

Watervliet Arsenal, Environmental and Safety Division -Watervliet, New York

Battelle Pacific Northwest National Laboratory -Richland, Washington

MSE Technology Applications Inc. -Butte, Montana

US Army Construction Engineering Research Laboratory -Champaign, Illinois

# **SODIUM HYDROXIDE RECYCLING AND RECOVERY AT WATERVLIET ARSENAL**

## **1.Introduction**

The U.S. Department of Defense (DOD) established the Environmental Security Technology Certification Program (ESTCP) to demonstrate the viability of innovative technologies that target environmental and waste reduction needs identified by DOD. The Sodium Hydroxide Recycling/Recovery System was chosen for evaluation under this program. The system uses filtration to remove suspended solids from caustic solutions used for cleaning and treating metal surfaces as part of the gun-tube manufacturing process. The system was designed to reduce potentially adverse environmental impacts while maintaining or improving product quality and decreasing costs. Demonstration testing was completed at the Watervliet Arsenal (WV A) in Watervliet, New York. This technology demonstration plan was prepared according to ESTCP guidance, which was developed to provide a standardized basis on which to compare innovative technologies for implementation within the federal sector. Effectiveness of this demonstration was evaluated in terms of technical, economic, and environmental significance.

### **1.1 Background information**

During Manufacturing of weapon systems large quantities of spent sodium hydroxide are produced by electroplating, surface finishing, and chemical milling/dissolution operations common to the Department of Energy (DOE), DOD, and private industry generating over 500,000 tons of sodium hydroxide waste per year. Sodium hydroxide comprises the largest volume of waste generated at U.S. Army depots and arsenals. Watervliet Arsenal generates multiple waste streams of spent concentrated caustic solutions that are used to clean dirt, rust, oil, grease, and other residue materials from metal surfaces before the processing steps in heat treatment and plating. Cleaning with alkaline solutions is the result of the chemical and physical processes. In the chemical process, certain contaminants form water- soluble soaps in the cleaning solution and in the physical process surfactants that are added to the solution to lower the surface tension of the contaminants. The increasing levels of contaminants that accumulate from the parts being cleaned limit the effective life of the sodium hydroxide solution. These contaminants reduce cleaning efficiency and reduce the quality of the metal finishing operation. Therefore, the solution must be periodically discarded and replaced with new cleaning solution. The high alkalinity (pH) of the spent solution requires disposal as a hazardous waste. This project demonstrated the use of an advanced filtration process to reduce and recycle sodium hydroxide solution to minimize hazardous waste and lower production costs.

### **1.2 Official DOD Requirement Statement**

The Sodium Hydroxide Recycling/Recovery System demonstration falls into the following official **DOD** requirements:

Army 2.3.1 - Treatment and Disposal Technology for Evolving Waste Materials.  
Priority: Medium

# **SODIUM HYDROXIDE RECYCLING AND RECOVERY AT WATERVLIET ARSENAL**

Army 2.3.C - Develop Recycle and Reuse Technologies.

Priority: Medium

Navy 2III.1. b - Advanced Destruction Capability for Hazardous Waste.

Priority: Medium

Navy 313.a Reuse/Recycle of Hazardous/Polluting Materials.

Priority: Medium

Navy 3.I.3.b Reuse/Recycle Waste Generated from Plating and Finishing Processes

Priority: Medium

## **1.3 Objectives of the Demonstration**

The primary objective of this demonstration was to confirm that the filtration technology, Vibratory Shear Enhanced Process (VSEEP), is an effective recycling and recovery process for prolonging the bath life of the caustic cleaning solution and reducing the volume of hazardous wastes. The testing was completed at the active finishing complex at WVA where the filtration unit processes spent caustic solutions generated from gun parts manufacturing. Data was gathered and documented to verify the performance and operability of the system. Specific performance objectives for this demonstration are presented in Section 4.1.

## **1.4 Regulatory Issues**

The Pollution Prevention Act of 1990 established pollution prevention as the nation's preferred approach to environmental protection and waste management, which is still true today. Although the Act does not mandate specific pollution prevention technologies, it does establish the prevention of the release of pollutants as the National Environmental Protection Policy. In 1992, the enactment of the Federal Facilities Compliance Act required that all federal facilities comply with all applicable hazardous waste laws and corresponding federal, state and local mandates. Executive Order (EO) 12856 issued in August 1993 required WVA and other DOD facilities to develop a plan to reduce the release of toxic chemicals by 50 percent by December 1999, utilizing 1994 as a baseline. New guidelines were required under EO 13101 and EO 13148 reaffirming and setting new procurement procedures and new threshold requirements for reduction. The New York State Department of Environmental Conservation (NYSDEC) and the U.S. Environmental Protection Agency (EPA) have requested WVA to reduce their current volume of disposed waste. In response to these mandates, WVA installed the Sodium Hydroxide Filtration Unit to recycle and reduce the volume of waste generated during the manufacturing process. Although the current surface treating operation poses no environmental threat, the waste stream must be managed as ~ hazardous waste under the Resource Conservation and Recovery Act (RCRA) for off-site disposal. The filtration system constitutes a recovery process that does not fall under the waste treatment regulations and does not require special environmental

# **SODIUM HYDROXIDE RECYCLING AND RECOVERY AT WATERVLIET ARSENAL**

permits. The reduction of this waste is highly desirable from a regulatory and economic point of view. The regulating official primarily responsible for the oversight of this operation was:

Mr. Clifton Van Guilder, PE  
Regional Solid and Hazardous Materials Engineer  
New York State Department of Environmental Conservation (NYSDEC)

## **1.5 Previous Testing of the Technology**

The V $\Delta$ SEP unit is commercially available, however, previous testing to recycle high pH caustic solutions had never been conducted.

# SODIUM HYDROXIDE RECYCLING AND RECOVERY AT WATERVLIET ARSENAL

## 2.0 Technology Introduction

V $\diamond$ SEP (Vibratory Shear Enhanced Process) was developed by **NEW LOGIC** as an enhanced liquid/solids separation system capable of providing dramatically improved filtration rates over traditional methods. The Series UP is a laboratory/pilot unit, designed for "in-plant/ evaluation and scale-up of this technology.

The unit is called the Series UP was created by combining the features of the earlier **NEW LOGIC** Series L and Series P V $\diamond$ SEP units. By changing and re-arranging various components, the operator of the Series UP can configure the system to operate as a Series L or as a Series P V $\diamond$ SEP unit.

The Series LIP, configured for "L mode" operation, is used to evaluate the performance of a single membrane in a V $\diamond$ SEP application. The "L mode" performance data and test results provide the information necessary to design the membrane modules for "P mode" operation of the UP or for large-scale V $\diamond$ SEP applications. The Series UP is generally shipped configured for "L mode".

The Series UP, configured for "P mode" operation, can be used for small-scale filtration applications or for further evaluation of V $\diamond$ SEP for large-scale applications.

The standard UP Filter Pack has 16.7 sq. ft. of membrane area. For higher capacity, the Series i system is available with 1600 sq. ft. or more of membrane area.

The purpose of this manual is to provide a comprehensive guide to the installation and use of the Series UP. These operating procedures have been developed through years of experience with V $\diamond$ SEP at the **NEW LOGIC** laboratory. When followed in the proper order, the sections detail step by step instructions for unpacking, installing, operating and configuring the Series UP. Where possible, potential trouble spots are pointed out. Also, a troubleshooting section guides the user through potential problems. Followed rigidly, these procedures will allow safe and reliable operation over many years. Failure to follow these procedures can result in poor performance, personal injury or irreversible equipment damage.

The "L mode" and "P mode" machine configurations require significantly different operating procedures. Please be certain that the section that is being referred to applies to the mode of operation that is being used.

Please read all applicable sections before operating the system

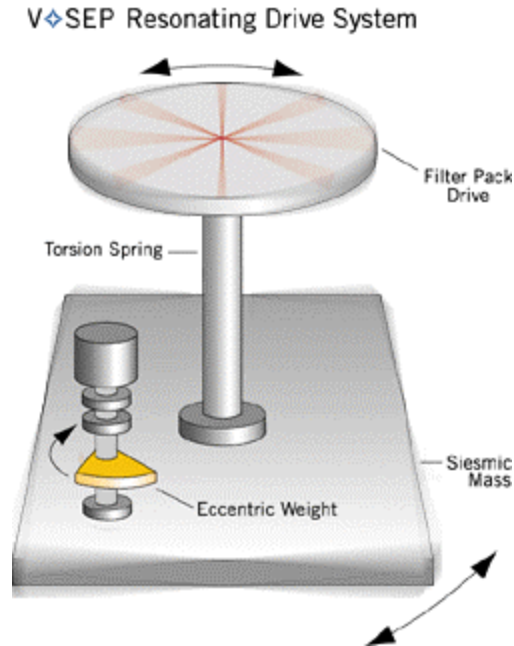
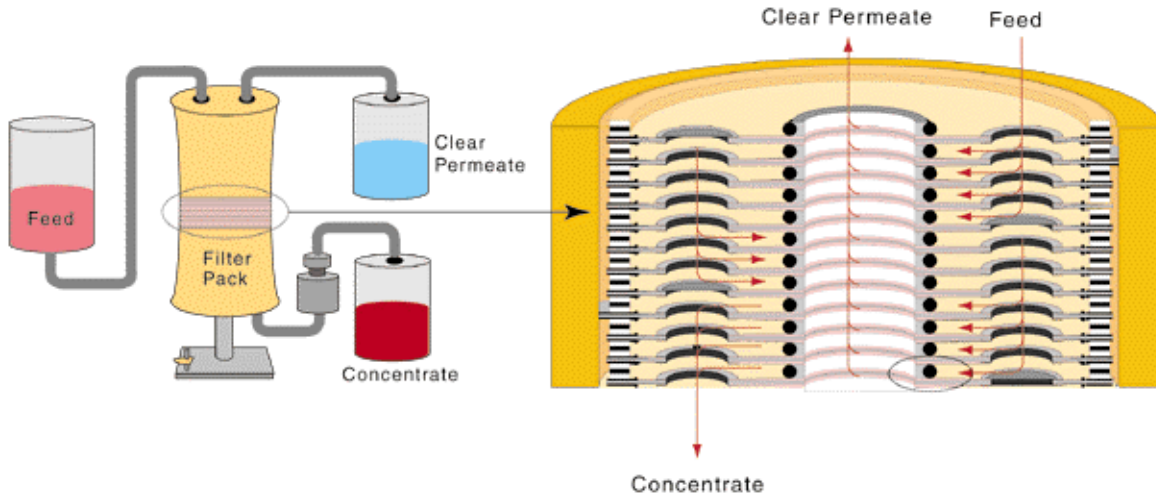
Please be advised that this machinery requires regular maintenance. Refer to the **MAINTENANCE** section of the manual.

If further assistance is required, contact **NEW LOGIC** Engineering

# SODIUM HYDROXIDE RECYCLING AND RECOVERY AT WATERVLIET ARSENAL

## 2.1 Technology Description

In a V $\diamond$ SEP system (see the figure below), the feed slurry remains nearly stationary between parallel membrane leaf elements while the leaf elements move to produce the shear. Membrane cleaning action is created by vigorously vibrating the leaf elements in a direction tangent to the faces of the membranes.



Using the V $\diamond$ SEP technology, a membrane separations system was demonstrated that exhibits superior antifouling characteristics to provide an effective recycling system for caustic cleaning applications.

Figure 2.1

# SODIUM HYDROXIDE RECYCLING AND RECOVERY AT WATERVLIET ARSENAL

The shear waves produced by the membrane's vibration cause solids and fouling materials to be lifted off the membrane surface and subsequently remixed with the bulk material flowing through the membrane stack. This high shear exposes the membrane pores, which maximizes fluid flow through the membrane. Flow rates are typically 3 to 10 times higher than the throughput of conventional cross-flow systems.

The V $\Delta$ SEP membrane filter pack consists of leaf elements arrayed as parallel discs and separated by gaskets. The disc stack resembles records on a record changer with membrane on each side. The disc stack is oscillated above a torsion spring that moves the stack back and forth approximately  $\frac{3}{4}$  to  $1\frac{1}{4}$  inches peak to peak. This motion is analogous to the agitator of a washing machine, but occurs at a speed faster than can be perceived by the human eye. The oscillation produces a shear at the membrane surface of about 150,000 inverse seconds (equivalent to over 200 G's of force), which is approximately 10 times the shear rate of the best conventional cross-flow systems. More importantly, the shear in a V $\Delta$ SEP system is focused at the membrane surface where it is cost effective and most useful in preventing fouling, while the bulk fluid between the membrane discs moves very little.

Because V $\Delta$ SEP does not depend on feed flow induced shearing forces, the feed slurry can become extremely viscous and still be successfully dewatered. The concentrate is essentially extruded between the vibrating disc elements and exits the machine once it reaches the desired concentration level.

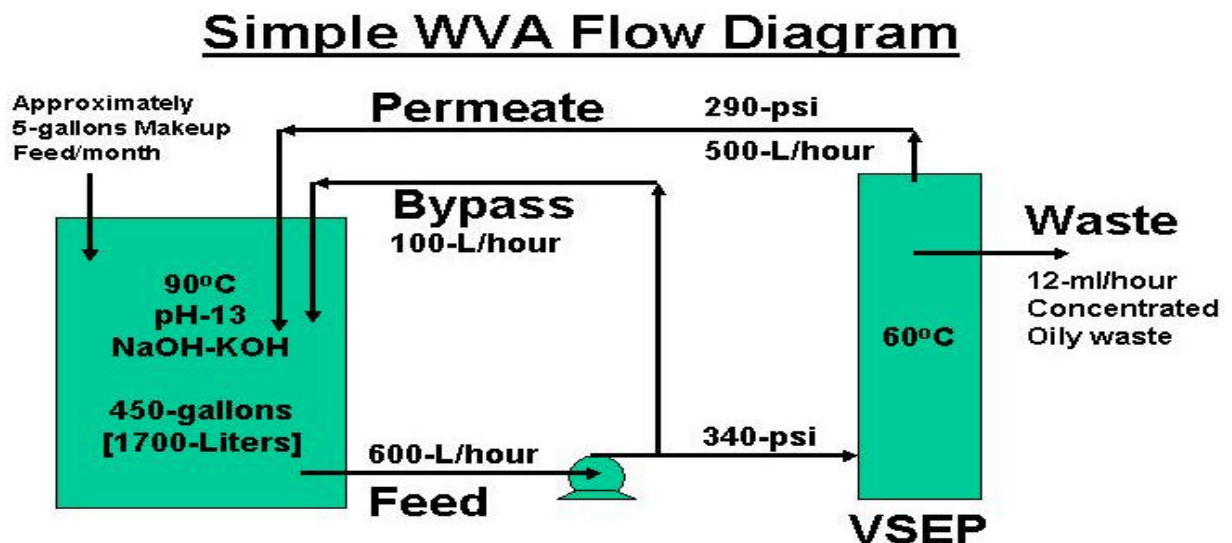


Figure 2.2 Process Flow Diagram

## **SODIUM HYDROXIDE RECYCLING AND RECOVERY AT WATERVLIET ARSENAL**

The demonstration phase of this project tested several types of filtration membranes amenable to strong, caustic solutions. These tests were conducted on spent solutions generated from the heat treatment process line. Primary contaminants in the spent solution were dirt, rust, scale, and quench oil.

### **2.2 Strengths, Advantages, and Weaknesses**

The Sodium Hydroxide Filtration System offers the advantage of effectively filtering highly caustic solutions. Today's standard technologies for solution separation, such as reverse osmosis, cannot operate efficiently in such harsh environments. The ability to filter highly caustic solutions will result in significant cost savings associated with disposal of potentially hazardous waste and purchase of replacement solution. Additionally, by maintaining a less contaminated cleaning solution, parts cleaning and subsequent plating processes showed an increase in process consistency with reduction in rework and scrap inventory. Strengths of the Sodium Hydroxide Filtration System are:

*Pollution Prevention* -By purifying the wash solution, the filtration system assists the DOD with waste management issues ( e.g., reduction in waste storage expenses, transportation fees, administrative and reporting burdens, and liabilities associated with accidental releases). The filtration process does not require additional chemicals or water, thus alleviating secondary waste. The process does not require special regulatory permitting.

*Advanced Materials of Construction* -The system is constructed using lightweight, custom configured, corrosion-resistant materials.

*System Operation* - VSEP provides two things: simplicity and performance. Simplicity derives from only two independent control parameters: shear and pressure. Shear is created by the amplitude of vibration of the filter pack and controlled by the drive motor speed. Pressure is created by the pump and is controlled by pump speed and/or flow regulation. The process can be designed to operate as a batch, semi-batch, or continuous operation for multiple or single waste streams, and can be built as a mobile or fixed system. The filtration process is a proven technology that is easily and safely operated and maintained with little impact from operation failure or variation in feed compositions. The addition of the vibration system enables the membrane filter to handle much higher particulate loading concentrations without membrane plugging and fouling.

The system offers no significant limitations. It requires less than 15 amperes of 208 -240 VAC 3-phase electrical power and a minimal amount of space for equipment installation. -.

### **2.3 Factors Influencing Cost and Performance**

Technology cost and performance are generally affected by waste characteristics and operating conditions. Factors influencing the Sodium Hydroxide Filtration Unit are:

# **SODIUM HYDROXIDE RECYCLING AND RECOVERY AT WATERVLIET ARSENAL**

- required feed flow rate; feed concentration and contaminants (i.e. dirt, rust, oil, grease, and other residue materials from metal surfaces and utility requirements).
- estimated life of a membrane pack is 12-18 months, depending on the alkaline solution and contamination material.

## **2.4 TECHNICAL OVERVIEW**

Beyond the flow-induced shear of conventional cross flow filtration, V $\phi$ SEP can produce extremely high shear on the surface of a membrane. The torsion vibration of a disk plate accomplishes this in a resonant spring-mass system. The membrane, which is attached to this plate, moves at amplitude of 5-10 degrees and a frequency in the range of 54 Hz. The fluid in the filter remains relatively motionless creating a highly focused shear zone at the wall {membrane surface}. Retained solids at the membrane surface are effectively removed by the shear allowing for higher pressures and higher permeate rates. Pressure is provided by a low flow pump, which circulates new fluid to the filter.

V $\phi$ SEP is simply two masses connected by Torsion Spring, which is excited at its natural resonant frequency. One mass, the Filter Pack, is lighter, holds the membrane(s), and moves with high amplitude. The other mass, the heavier Seismic Mass, moves with smaller amplitude proportional to the ratio of the two masses. The use of two masses allows the system to resonate without attachment of the device to a rigid surface.

The excitation is created by an AC motor controlled by a variable frequency, solid state speed controller. The motor spins an Eccentric Weight coupled to the Seismic Mass. Since the eccentricity of the weight induces a wobble, the Seismic Mass begins to move as the motor speed increases. This energy is transmitted into the Torsion Spring and begins to move the Filter Pack at the top, but at 180 degrees out of phase. As the motor speed approaches the resonant frequency, the amplitude of the moving Filter Pack reaches a maximum, and greater motor speed will only decrease the amplitude. V $\phi$ SEP is run below the maximum amplitude to reduce spring stress and ensure an almost infinite spring life.

To allow for free movement, the entire system rides on isolators. Solid piping to the Filter Pack assembly is clamped to the Torsion Spring and is removed at the node (zero amplitude) point. Flexible piping is use at the top of the Filter Pack. For safety and sound reduction, the entire assembly is enclosed in a cabinet.

When the Series UP is configured for "L mode" operation, the Filter Pack consists of a single membrane enclosed in a "Clamshell" assembly. The Feed (Process In) and Concentrate Exit (Process Out) piping connect at the bottom of the Filter Pack. The Filtrate (Permeate) piping connects at the top of the Filter Pack. The unit operates with continuous flow, limited by the "pump ability" of the feed slurry through the system.

When the Series UP is configured for "P mode" operation, the Filter Pack consists of a stack of membrane elements and spacers. Feed is pumped in at the top of the Filter Pack. The Permeate exits at the top, and the Concentrate exits at the bottom of the Filter Pack.

## SODIUM HYDROXIDE RECYCLING AND RECOVERY AT WATERVLIIET ARSENAL

Using a time cycled output valve can control the density of the Concentrate. By adjusting the duty cycle of the valve the concentrate density can be optimized. The valve may also be controlled to maintain a constant vibration motor load (or constant filter pack weight).

V $\diamond$ SEP provides two things: simplicity and performance. Simplicity derives from only two, independent control parameters: shear and pressure. Shear is created by the amplitude of 'vibration of the Filter Pack and controlled by the drive motor speed. Pressure is created by the pump and is controlled by pump speed and/or flow regulation.

September 1998



# SODIUM HYDROXIDE RECYCLING AND RECOVERY AT WATERVLIIET ARSENAL

## Crossflow

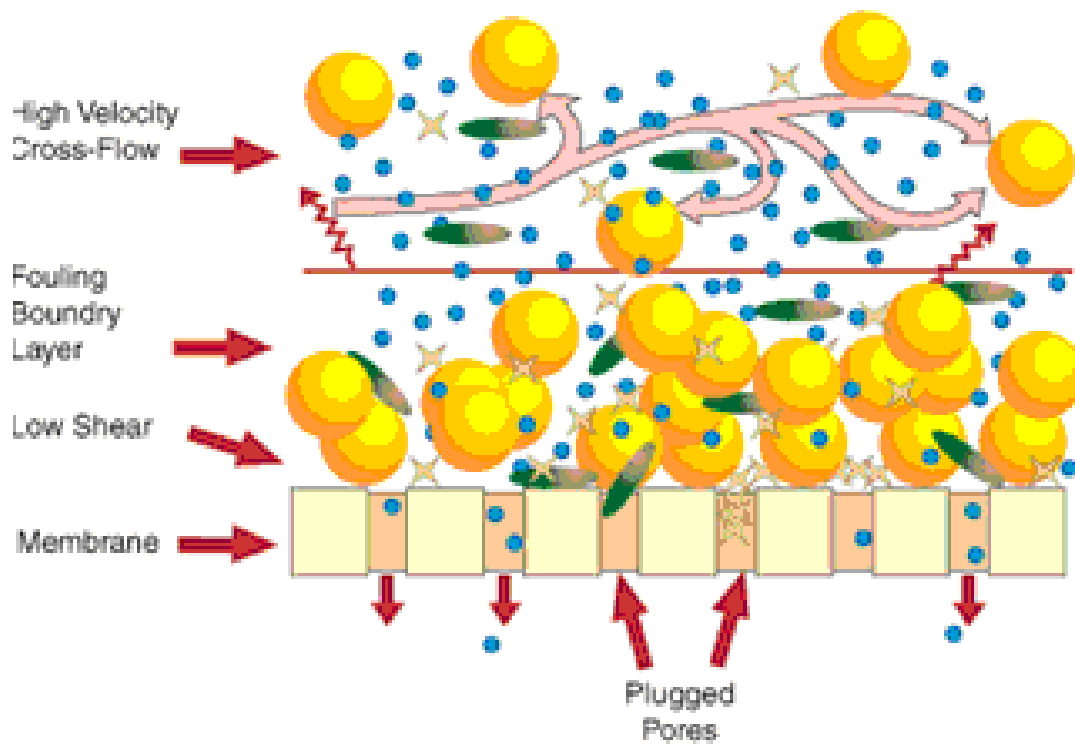
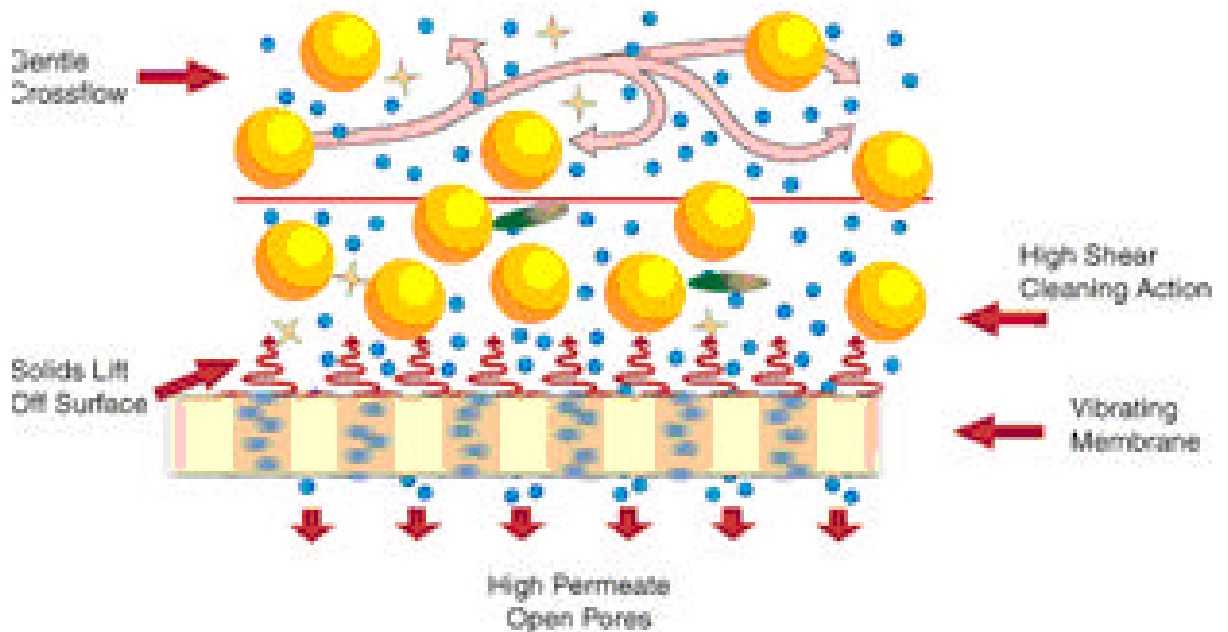


FIGURE 2.3

## V+SEP



# SODIUM HYDROXIDE RECYCLING AND RECOVERY AT WATERVLIET ARSENAL

## 3. Site Facility Description

### 3.1 Background

The Watervliet Arsenal (WVA) was selected for this demonstration based on the type and volume of waste generated, the capacity limitations of their waste treatment plant, and the emphasis on complying with waste minimization goals mandated by DOD. The New York State Department of Environmental Conservation is also encouraging the demonstration to reduce the disposal volume of caustic waste solutions generated by WVA.

### 3.2 Site/Facility Characteristics

3.2.1 Watervliet Arsenal (WVA) is located in Watervliet, New York and is an Army owned and operated facility that began armament manufacturing in 1813. A map showing the location of Watervliet is shown in Figure 3.1. WVA continues to manufacture products for the military ranging from rocket mortars to battleship guns. WVA consists of two primary areas: (1) Main Process Area where manufacturing and administrative operations encompass 125 acres and; (2) Siberia area which is 15 acres and is mainly used for storage. Land use surrounding WVA is primarily residential, with some light to medium industrial facilities along the western boundary. This demonstration took place in Building 35 in the heat treat area. This area is where components are cleaned with caustic solutions, rinsed, and heat treated. The facility location allows access to spent caustic solution, drain connections to the caustic waste lines, electrical power and sufficient floor space for equipment installation. During 1995, WVA produced and disposed 150 tons of spent solutions at a cost of approximately \$160,000. The major cost drivers associated with this activity involved hazardous waste disposal exceeding \$70,000 and the purchase of replacement NaOH at approximately \$54,000, with an additional \$36,000 for labor and associated costs. With future escalation of hazardous waste disposal cost, waste acid recycling represents an attractive alternative and tremendous cost saving opportunity to WVA, as well as an approach for complying with mandated pollution prevention goals.

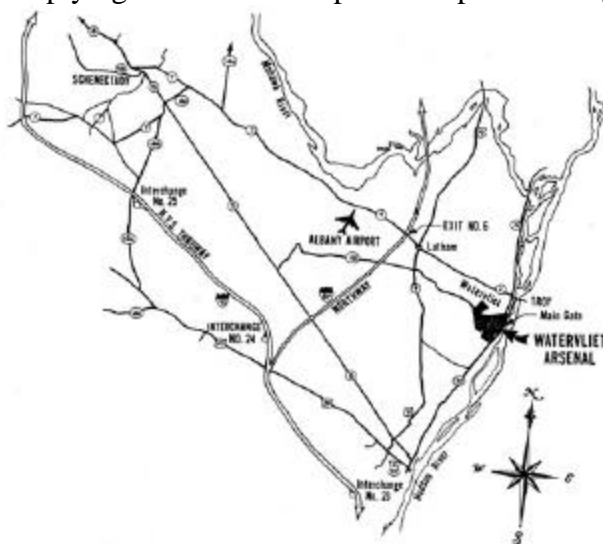
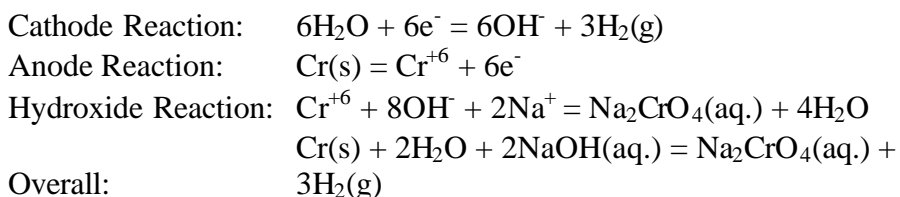


Figure 3.1 Map showing Watervliet.

## SODIUM HYDROXIDE RECYCLING AND RECOVERY AT WATERVLIET ARSENAL

3.2.2 The Corpus Christi Army Depot (CCAD) is the Army's only facility for the repair and overhaul of rotary wing aircraft. CCAD is a major contributor of the Army, Navy, Marine Corps, and Air Force readiness through repair, overhaul, and maintenance of a wide variety of helicopters as well as related engines and components.

The CCAD facility electro-strips hard chrome plating from stainless steel and steel parts, for refurbishment, according to MIL-STD-871, solution #6 (68 to 82 grams sodium hydroxide per liter of water, at 6 volts anodic, and room temperature; 60 – 90°F). This process (also known as reverse current stripping, as well as anodic stripping) oxidizes the metallic chrome plating to hexavalent chromium. The process requires bath agitation so that the chemicals are mixed at the part surface. These chemicals transport the chrome from the surface of the part and into the bulk fluid. The hydroxide anion complexes the chromate from the part surface, and dissolves it into the solution as sodium chromate ( $\text{Na}_2\text{CrO}_4$ ), which gives the solution a distinctive yellow color. Although the exact mechanism of this reaction could not be found in the literature, the following pathway is possible, leading to the final products:



Good agitation of the solution is required due to pockets or blind holes containing hexavalent chromium can react into its fairly strong acid form [i.e.,  $\text{Cr}^{+6} + 6\text{OH}^- = \text{H}_2\text{CrO}_4(\text{aq.}) + 2\text{H}_2\text{O}$ , with a PKa of 0.74], which can cause severe etching of the base metals.

The stripped chromium dissolves into solution, thus changing the bath salt concentration. The buildup of chromate salts is detrimental to the process, and without purification, the bath must ultimately be discarded and remade. The warning signs of a poisoned solution are slow stripping rates, high-energy consumption, and damage to the part substrate.

As the time spent to strip the chrome plating increases, the likelihood for uneven stripping occurs, which can result in base metal etching to an unacceptable degree. Hard steels can withstand the etching action of anodic stripping longer than unhardened steels. Also, under the highly alkaline conditions, and with time, some of the chromium will reduce valence to trivalent chromium, and thereby precipitate to the bottom of the tank as hydroxide sludge [information excerpted from a plating and metal finishing news group].

Chromate solubility in a pH 14 solution of NaOH is estimated to be in the range of 450 to 800 g/L at temperatures ranging from 85°F to 212°F. Iron and nickel oxides in solution will significantly reduce chromate solubility, as will the reduction in pH as the electrolyte is consumed [Xing Zou, Yi Zhang, et al., *Journal of University of Science and Technology Beijing* (English Edition), 7(2000), No.2, pp.79-156].

# **SODIUM HYDROXIDE RECYCLING AND RECOVERY AT WATERVLIET ARSENAL**

## **4.0 Demonstration Approach**

### **4.1 Performance Objectives**

The objective of this demonstration is to determine the ability of the VØSEP Filtration System to recover and recycle spent caustic washing solutions. The system must meet the following criteria:

\* Remove sufficient quantities, estimated as less than 2% of the total volume, of the alkaline solution contaminants in order to recycle the cleaning operation permeate as a caustic solution or a caustic solution base. It is anticipated that some addition of fresh caustic/surfactant will be required at regular intervals, based on volume. Contaminant levels will vary depending on workload. Bath specifications for the caustic solution contains raw sodium hydroxide at a concentration of between 60 and 120 grams of NaOH per liter. The pH is maintained at 12 or greater.

MSDS and Caustic Cleaner Product Bulletin can be reference in Appendix C.

\* Demonstrate the ability to regenerate the washing solution at thru puts up to 3 gallons per minute (gpm) as a minimum flow requirement through the process.

\* Demonstrate safe and economical operation with minimal operator oversight.

### **4.2 Demonstration Setup, Commencement and Operation**

The prototype system was installed beside the wash tanks in the Minor Plating and Heat Treatment Building at Watervliet Arsenal and required three phase, 208 -240 V AC for operation. The system is mobile and easily moved to locations. The space it will occupy will be near the tank and will need no additional work to locate.

The system operated in a continuous mode. Contaminated caustic solutions from the heat treat wash bath caustic tank will be pumped through the filtration system with the permeate solution returned to the tank. It will take 4 to 5 tank turnovers to clean the tank but it will allow the manufacturing process to continue. The feed, permeate and concentrate solutions will be sampled at ports provided by the manufacturer on the unit and analyzed.

Testing of the membranes for the specific solution was performed on 6 different membranes.  
(SEE APPENDIX G)

This technology was shared with Corpus Christi Army Depot (CCAD). They had expressed great interest in recycling their alkaline solutions and asked for actual membrane testing on their site.

# **SODIUM HYDROXIDE RECYCLING AND RECOVERY AT WATERVLIET ARSENAL**

**Contaminants.** The system is designed to filter and purify caustic sodium hydroxide solutions for reuse. The system, as tested here, is for recycling spent caustic solutions that have degraded during the cleaning processing. Contaminants are oils, grease, metal fragments, grit, and scale that are generated during fabrication and heat treatment.

**Process Waste .** During the operation of the filtering unit approximately 2% of the total 300 gallons bath will be collected as concentrated oily hazardous waste. This must be shipped off post to be treated.

**Factors Affecting Technology Performance.** Contaminant type and concentration may affect the filtration efficiency of the system. The amount of contaminant loading on the filter membrane will affect the filtration rate as will physical and chemical degradation of the membrane. (SEE APPENDIX G)

**Reliability.** The design of the unit is simple, and the materials used to construct the unit have been proven in the commercial sector. The system uses a new method of vibratory shear to keep the membrane from fouling. This technology is new and endurance testing has not occurred . Mechanical failure of the filtration system is not expected. The use of advanced corrosion-resistant materials allows the unit to function in harsh environments. The system is reliability. The design of the unit is simple, and the materials used to construct the unit have a proven design for maximum flow rate and contaminant concentration. If these values change, they will most likely influence the system's efficiency and processing time.

**System Operation.** The system design requires minimal operator assistance and minimal maintenance. Once the system is installed, the only inputs to the system are electricity and spent caustic solution. The system is operated through a graphical man-machine interface. A touch screen provides the operator access to the system in the manual mode. A Programmable Logic Controller (PLC) uses data fed to it from the system to control the process. Minimal instruction is needed to operate the system. Monitoring is required at start-up, shutdown, and at the end of a batch run and intermittently during operation. Safety controls and alarms are discussed in the system's operations manual. The operation of the system will not interfere with the manufacturing cleaning process. Work can continue.

The system operation features include:

- \*Pressure transducers and controllers to automatically shut the system in the event of system plugging or line failure.
- \*Flow indicators and controllers to automatically shut the system down in the event of a line failure. Also negated the need for measuring flow manually with a graduated cylinder.
- \*Temperature indicators to warn the user in the event if an over temperature situation for a given membrane.
- \*pH indicator to monitor and warn the user in the event of a high pH condition for a given membrane

## **SODIUM HYDROXIDE RECYCLING AND RECOVERY AT WATERVLIET ARSENAL**

- \*Level switch to automatically shut the system down when the concentrate vessel is full.
- \*Pre-assembled filter pack such that a membrane pack can be changed out in a manner of minutes instead of hours
- \*Transformer to make the system useable in either 440V or 240V wired facilities. Cart to make the system transportable if desired.
- \*Water addition tank to either flush the membrane or provide make-up solution for depleted surfactants, additives, or formula. Membrane flushing during processing will occur at preset conditions.
- \*Additional valves to route fluid flow as desired.

**Variability** .The Sodium Hydroxide Filtration System is applicable in any situation where filtration can affect the recycling or purification of a waste. However, the economic variability of the system is dependent upon the waste source volume.

This dependency, with respect to spent caustic solutions, will be determined during this demonstration.

Reference appendix G for Membrane Selection Process.

**Off-the-Shelf Procurement.** The prototype system uses a proprietary material manufacturing process developed by New Logic International of Emeryville, California. All other equipment including valves, controls and piping are off-the-shelf items.

**Maintenance.** Maintenance on the system is discussed in the Operations Manual for the unit. This document is attached as Appendix B .

**Scale-up Issues.** This system is a full-scale unit designed to process up to three gpm of waste solution. If needed, scale-up can be accomplished by the addition of parallel units or by procuring a larger unit from the manufacturer.

Prior to the start of the demonstration additional Pollution Prevention initiatives were initiated to reduce waste in the area with co-funding. The controls and operations of the facility were automated reducing the loading in the baths on the main process line. This effectively reduced the requirements to the heat treatment tank. The installation allowed for improved rinsing of parts in the Magnesium Phosphate line reducing the loading of contaminants being introduced into the process-cleaning tank. Through the initiation of this project waste generation was reduced by 30% annually. Another benefit achieved was an improved product and improved throughput on the manufacturing line.

### **4.3 Sampling Procedures**

Sampling plan and procedures for this demonstration are presented in the Sodium Hydroxide Demonstration Plan. Performance testing for this demonstration was conducted August 3 to August 11,1999. Testing of the membranes was conducted in December 1998 and again from February through March 1999.

## **SODIUM HYDROXIDE RECYCLING AND RECOVERY AT WATERVLIET ARSENAL**

At the beginning of each test run of the membranes, concentrations were measured at the system inlet or outlet to determine a "baseline." After that, these concentrations were measured at the system outlet to determine the efficiency of the recycling/recovery process to concentrate and purify the process solution. Flow rate was measured to control the operating conditions. For each batch, the following operational and sampling sequence was followed:

Prior to equipment start-up, all sampling containers were labeled.

Samples were taken from the inlet and outlet ports and analyzed for pH, total residue, alkalinity, surfactant, oil and grease. These concentrations represent the initial values.

The filtration system processes the entire 300 gallons of spent cleaning solution from the bath in each run. The system made 4 to 5 runs over several days in order to clean the bath. This was done so the cleaning of parts could continue.

Samples were collected from the outlet port and analyzed for pH, total residue, alkalinity, oil, grease and surfactant. These samples represent the final values.

The following field quality assurance (QA) samples were also taken:

Field Duplicate. Consisted of two samples collected consecutively at the same location and placed in separate bottles for separate analysis. These samples were collected at a frequency of one per 20 samples or one per sampling event whichever was more frequent.

Initial Calibration Verification (ICY) and Continuing Verification (CCY). These samples were used to verify the calibration of instruments and to verify the calibration curve for a particular method.

Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB). These two blanks were used to determine the existence and magnitude of contamination problems caused by instrument memory.

Spikes. Spike sample analysis is designed to provide information about the effect of the samples matrix on the digestion and measurement methodology.

These field QA samples were used to evaluate data quality

## SODIUM HYDROXIDE RECYCLING AND RECOVERY AT WATERVLIET ARSENAL

### 4.4 Analytical Procedures

Benet Laboratories performed all sample analytical testing. Benet Laboratories is located at WV A and is government owned and operated. Benet Laboratories is a division of the Close Combat Armaments Center (CCAC), which in turn, is part of the Department of Army's Armaments Research, Development and Engineering Center (ARDEC). Benet Laboratories provides support to research and development activities conducted at WV A and other DOD facilities.

Methods for sample analysis are shown in Table 4.2. These methods are all standard EPA methods.

Analyte	Matrix	Holding Time	Sample Size & Hold Time	Method
pH	Aqueous	Analyze Immediately	250 ml HDPE	Method 424 Standard Method for Examination of water and Wastewater
Total Solids	Aqueous	Store @ 4° C 7 Days	250 ml HDPE	Method 424 Standard Method for Examination of water and Wastewater
Alkalinity	Aqueous	Store @ 4° C 14 Days	250 ml HDPE	Method 424 Standard Method for Examination of water and Wastewater
Oil & Grease	Aqueous	Store @ 4° C pH < 2 H <sub>2</sub> SO <sub>4</sub> 28 Days	2 Liters	Method 424 Standard Method for Examination of water and Wastewater
Surfactant	Aqueous	Store @ 4° C 14 Days	10 micro-liters	ASTM E168 Standard Practice for General Techniques of Infrared Qualitative Classification by Infrared Absorption

**Table 4.2. Analytical Methods**

# SODIUM HYDROXIDE RECYCLING AND RECOVERY AT WATERVLIET ARSENAL

## 5. Performance Assessment

### 5.1 Performance Data

A membrane based system for recovery and recycling caustic cleaners has been successfully deployed at Watervliet Arsenal.

Alkaline cleaning processes are typically batch operations and as such, oils, grease and soils collect in the cleaning tank and progressively decrease cleaning efficiency. A typical caustic cleaning solution becomes unusable due to this contamination long before the alkalinity builders, surfactants and the additives are actually consumed.

The application at Watervliet Arsenal was to recycle caustic bath solutions that are used to remove oils and particulate matter from parts used in the manufacture of large weapons. These parts must be cleaned prior to heat treatment and finish coating, thus cleaning is critical to adhesion and the quality of the finish coating, and is directly linked to incidents of rework and scrap.

A Vibratory Shear Enhanced Processing (V $\diamond$ SEP) system, a membrane based recycling process, was installed at Watervliet Arsenal with excellent results. The V $\diamond$ SEP process makes use of a mechanical arm to vibrate a circular membrane pack in a twisting motion. These motions produce shear waves that propagate sinusoidal from the surface of the membrane such that soils and solids do not have the opportunity to adhere and foul the membrane. They are literally bounced off the membrane surface.

The membranes for this system are in a pack that would only need replacement on the order of every year to two years. Change out is relatively simple and can be accomplished in approximately 2 hours. Our V $\diamond$ SEP machine with a 4 ft by 5 ft footprint accommodated 16.7 sq ft of membrane surface area.

The cleaning of the 300 gallons in the heat treat cleaning tank took about 4 to 5 tank turnovers to bring it back to the original state. This is the result of returning the permeate solution back to the original tank so production personnel can continue to use the tank. The flow rate thru the V $\diamond$ SEP unit averaged 3gpm.

During the operation of the unit many samples were taken of the feed, permeate and the concentrated waste solutions. Figure 5.1 shows 6 samples lined up, from left to right, five of these are feed samples that were taken at 3-hour intervals. They show the effect of the cleaning process on the main process tank. The first sample shows the condition of the feed solution at the start and each sample after shows the effect of the V $\diamond$ SEP unit processing the feed solution and removing the oil and dirt. It takes about 4 to 5 tank volume turnovers to bring the 300-gallon tank back to near the original state. This is the result of returning permeate back to the main tank so the manufacturing process could continue.

The last sample on the right shows the permeate solution after it passes thru the membranes. If

## **SODIUM HYDROXIDE RECYCLING AND RECOVERY AT WATERVLIET ARSENAL**

we had continued to process the feed solution we could have brought the tank back to this clarity and color.

Figure 5.2 shows an enlargement of the first sample, the original condition of the feed tank and the last feed sample, this clearly showing the positive effect of processing the solution thru the VØSEP unit.

Figure 5.4 shows, from left to right, a concentrated waste sample, a feed sample and a permeate sample.

These Photographs are visible records that show the VØSEP membranes remove dirt and oil.

### **5.2 Data Assessment**

All the feed and permeate samples were tested for pH, total solids, alkalinity, oil & grease and surfactants. We encountered great difficulty with the oil & grease analyses using Method 502A of the Standard Method for Examination of Water and Wastewater. We tried very hard to find an alternative test and failing at this we resorted to infrared analyses per ASTM E168 and D2357 to prove that contaminants were being removed and the good elements of the cleaning solution were remaining. IR spectral analyses are qualitative and not quantitative.

Further investigation and consultation with private industry revealed that this is a common problem, that oil contamination interferes with standard analytical techniques that would quantify what components of an aqueous solution were being retained or passed through a particular membrane. One company had determined that IR spectral analyses could be used to identify the occurrence of some additives, but not all. They said there is no simple analytical method currently available to determine bath makeup solutions after recycling operations. Their current methodology is to add concentrate in dilute quantities, but they admitted there is no way to accurately determine what the dilution factor might be without obtaining empirical data for each individual bath. Also a problem with adding concentrate is that there's always the potential for precipitating key elements of the solution. There is at present no method to completely answer the question, is there a key element missing from the recycled solution? We tried to establish a CRADA with this company to further develop a testing methodology together for determining caustic bath usability, but they were unwilling to do so.

The data developed from our laboratory analysis is enclosed (Tables 5.1 and 5.2) after the three pictures of the samples. The \* under the oil & grease columns indicate samples that were especially troublesome.

On the first data sheet the suffix letter denotes samples taken each day, starting of course with A. This data was used to evaluate different membranes performance and then to select the best membrane for our application. The VØSEP unit was in the L processing mode during the gathering of this data.

On the second data sheet the prefix letters on the sample # columns stand for following: F for a feed sample, P for a permeate sample and C for a concentrate sample. The suffix letter again

## **SODIUM HYDROXIDE RECYCLING AND RECOVERY AT WATERVLIET ARSENAL**

denotes samples taken each day. The VØSEP unit was in the P processing mode during the gathering of this data.

Next (Figures 5.4-5.7) is the IR spectral analysis, the first one is a control sample which is virgin material, the second is a feed sample, third is a permeate sample and fourth is a concentrated waste sample. At the 400 to 1700 is the surfactant/additives range, oil and grease if in the IR is at the 950 to 1250 ranges and at the 2300 peak is excess CO<sub>2</sub> which wasn't purge properly between samples. The CO<sub>2</sub> means nothing. What is significant are the little peaks in the oil and grease range in the spectra. Some of these are oil; some are oxidized oil suggesting either an oxidized sulfur or nitrate group. The fourth spectrum, the concentrated waste sample, naturally shows the greatest amount of oil and grease in this range. The control sample shows none and the permeate sample shows very little.

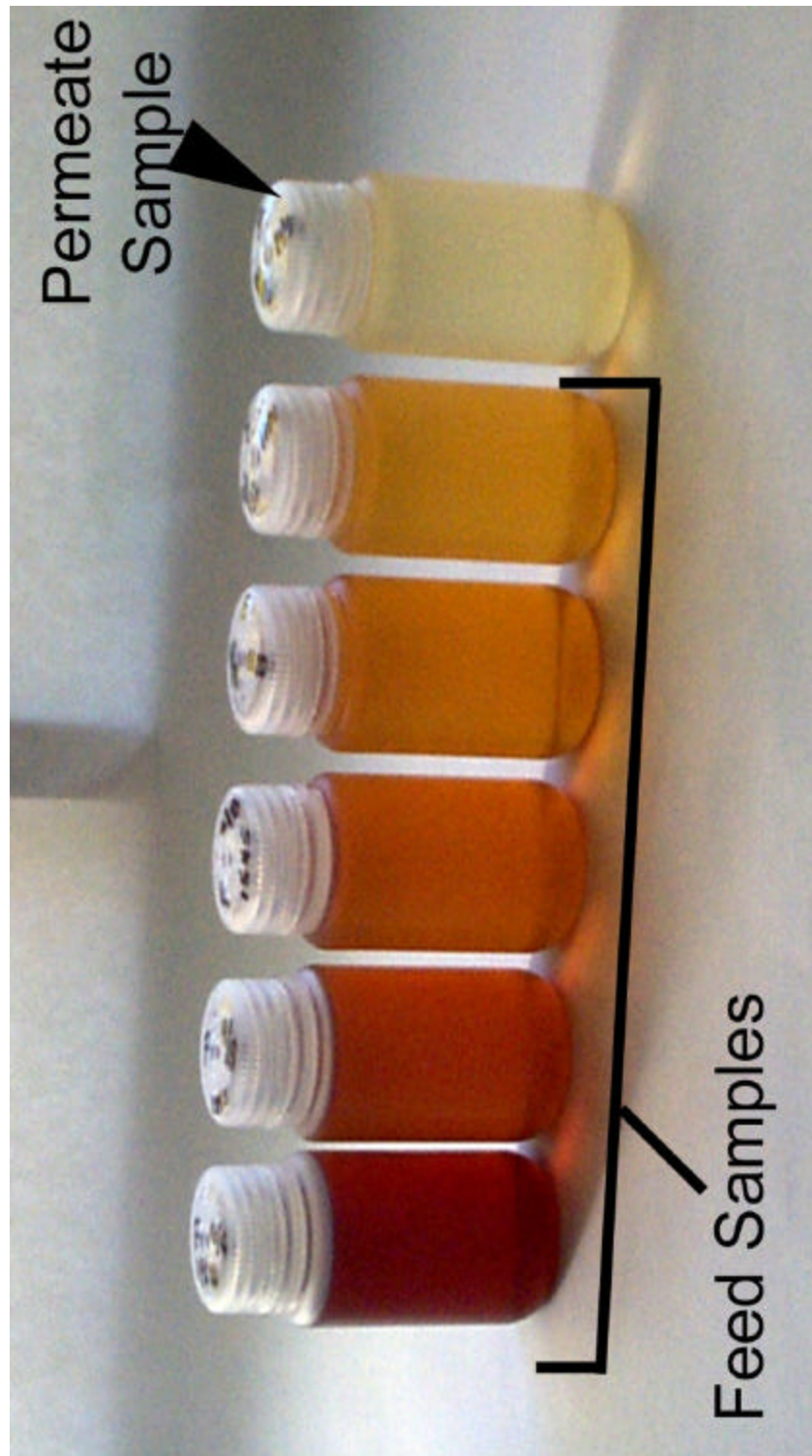
Although the analysis tells us what is and isn't in the solution, it can't tell us how much.

### **5.3 Technology Comparison**

The demonstration proved the VØSEP technology to be highly effective for recycling high pH solutions of the type typically found in metal finishing operations. The membranes did not become plugged, nor are they prone to failure. The system is relatively easy to set up and with a few minor changes in the operator interface, can be made extremely easy to use. The life of the membranes is estimated at 1 to 2 years when cleaned by the VØSEP system and this far exceeds other filtering systems. Early efforts to maintain performance of membranes led to the development of cross-flow filtration to generate tangential shear at the membrane surface but even the most robust system cannot keep the membrane clear for more than a few days of operation. Membrane life can be extended by back flushing through the membrane with toxic chemicals but this is costly and generates another toxic waste. The VØSEP system does not depend on feed flow induced shearing forces, but the shear is focused at the membrane surface where it is most cost effective and most useful in preventing fouling.

Testing of spiral wound membranes and ceramic membranes were not feasible for testing in this program. The cost of the ceramic was considerably higher and with the change out for testing of poor size would not have been economically feasible. The rapid change out of membranes and relatively economical costs provided the project with rapid and economical comparisons between different membranes, pour size and material.

# SODIUM HYDROXIDE RECYCLING AND RECOVERY AT WATERVLJET ARSENAL



**Figure 5.1**

**SODIUM HYDROXIDE RECYCLING AND RECOVERY  
AT WATERVLIET ARSENAL**



**Figure 5.2**

# SODIUM HYDROXIDE RECYCLING AND RECOVERY AT WATERVLIET ARSENAL



**Figure 5.3**

# SODIUM HYDROXIDE RECYCLING AND RECOVERY AT WATERVLIET ARSENAL

**Table 5.1**

<i>SAMPLE #</i>	<i>Ph</i>	<i>ALKALINITY</i> (g/l)	<i>TOTAL SOLIDS</i> (g/l)	<i>OIL &amp; GREASE</i> (g/l)
120298A	8.75	0.08		0.04
120298B	13.13	43.54	95.77	4.35*
121598A	13.03	35.64	86.15	0.10
121598B	13.04	36.97		0.08
121598C	12.98	38.76		3.88*
121598D	12.98	38.29	89.69	2.66*
121698A	13.00	31.94	71.09	0.08
121698B	12.96	34.01	79.01	1.76
CONTROL	13.14	33.73	72.93	6.67*
021999A	12.69	13.83	35.76	1.10
021999B	12.75	13.11	31.57	0.11
022399A	12.75	15.20	37.01	1.02
022399B	12.76	14.67	31.32	0.16
022499A	12.74	15.68	38.34	1.33
022499B	12.74	16.11	38.43	1.44
022499C	12.71	15.05	32.11	0.31
022499D	12.71	15.62	48.03	7.51*
022499E	12.75	16.72	33.69	0.13
022499F	12.69	15.20	41.83	2.09*
022499G	12.72	14.06	42.38	0.25
022599A	12.66	14.76	36.67	0.95
022599B	12.70	14.14	30.90	0.07
022599C	12.70	15.68	38.38	0.83
022599D	12.72	14.95	31.86	0.73*
022599E	12.63	14.17	34.40	0.74
022599F	12.66	13.09	28.65	1.09
030199A	12.64	14.82	35.88	1.11*
030199B	12.66	13.87	35.41	1.30*
030199C	12.69	14.52	35.07	0.58*
030199D	13.05	15.77	39.83	1.26
030199E	13.02	15.58	38.01	1.75*
030199F	13.01	14.82	39.29	1.15*
030199G	13.02	13.68	44.34	0.72*
030299A	13.02	15.20	48.00	0.99
030299B	13.00	14.25	45.82	0.60
030299C	13.09	13.11	44.63	1.17*
030299D	13.02	14.63	43.10	1.11
030299E	13.07	13.68	37.95	2.10*
030399A	13.04	13.87	38.25	0.08
030399B	13.03	14.06	41.45	0.15*
030399C	12.99	14.63	36.80	1.15
030399D	12.99	14.63	37.80	0.96
030399E	13.03	13.49	34.41	0.11
030399F	12.99	14.44	36.41	1.02
CONTROL	13.12	33.10		
030499A	13.01	13.87	30.29	0.18*
030499B	12.97	14.82	36.55	0.72
030499C	13.02	13.87	30.24	0.20*
030499D	12.98	14.82	36.20	0.83
030499E	13.01	13.87	30.35	0.19*
030499F	12.98	14.63	35.79	1.02
CONTROL		33.44	85.69	

**SODIUM HYDROXIDE RECYCLING AND RECOVERY  
AT WATERVLIET ARSENAL**

<b>SAMPLE</b>	<b>pH</b>	<b>OIL &amp; GREASE g/L</b>	<b>ALKALINITY g/L</b>	<b>TOTAL SOLIDS g/L</b>
F080599A	13.55	6.941*	25.02	59.036
P080599B	13.63	0.185	24.47	46.806
F080699A	13.58	<0.01	28.03	58.522
P080699B	13.69	<0.01	25.61	49.782
F080999A	13.62	3.333*	25.21	53.618
P080999B	13.61	1.131*	25.84	51.256
C080999C				313.170
F081099A	13.67		25.80	58.618
P081099B	13.65		25.84	48.916
F081099C	13.65		26.49	61.754
P081099D	13.65		26.20	58.722
F081199A	13.65	5.043	25.14	54.150
P081199B	13.62	<0.01	25.25	64.866
F081199D	13.62		25.14	55.522
P081199E	13.63		25.18	71.326
F081699A	13.62		24.55	54.358
P081699B	13.58		24.53	52.268
F081799A	13.60	11.580	23.56	51.940
P081799B	13.61	0.342	23.47	48.350

**Table 5.2**

# SODIUM HYDROXIDE RECYCLING AND RECOVERY AT WATERVLJET ARSENAL

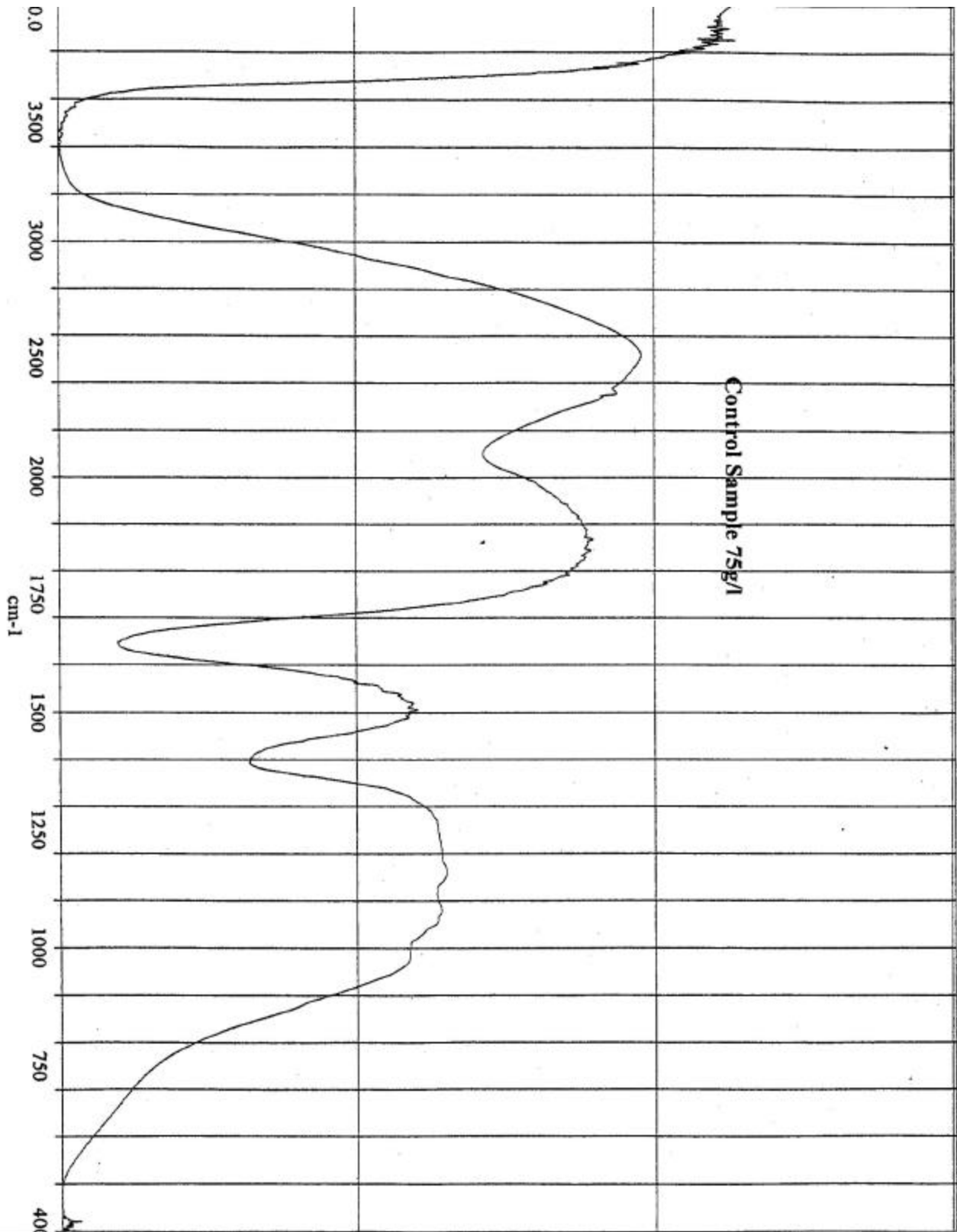


Figure 5.4 Control Sample

# SODIUM HYDROXIDE RECYCLING AND RECOVERY AT WATERVLJET ARSENAL

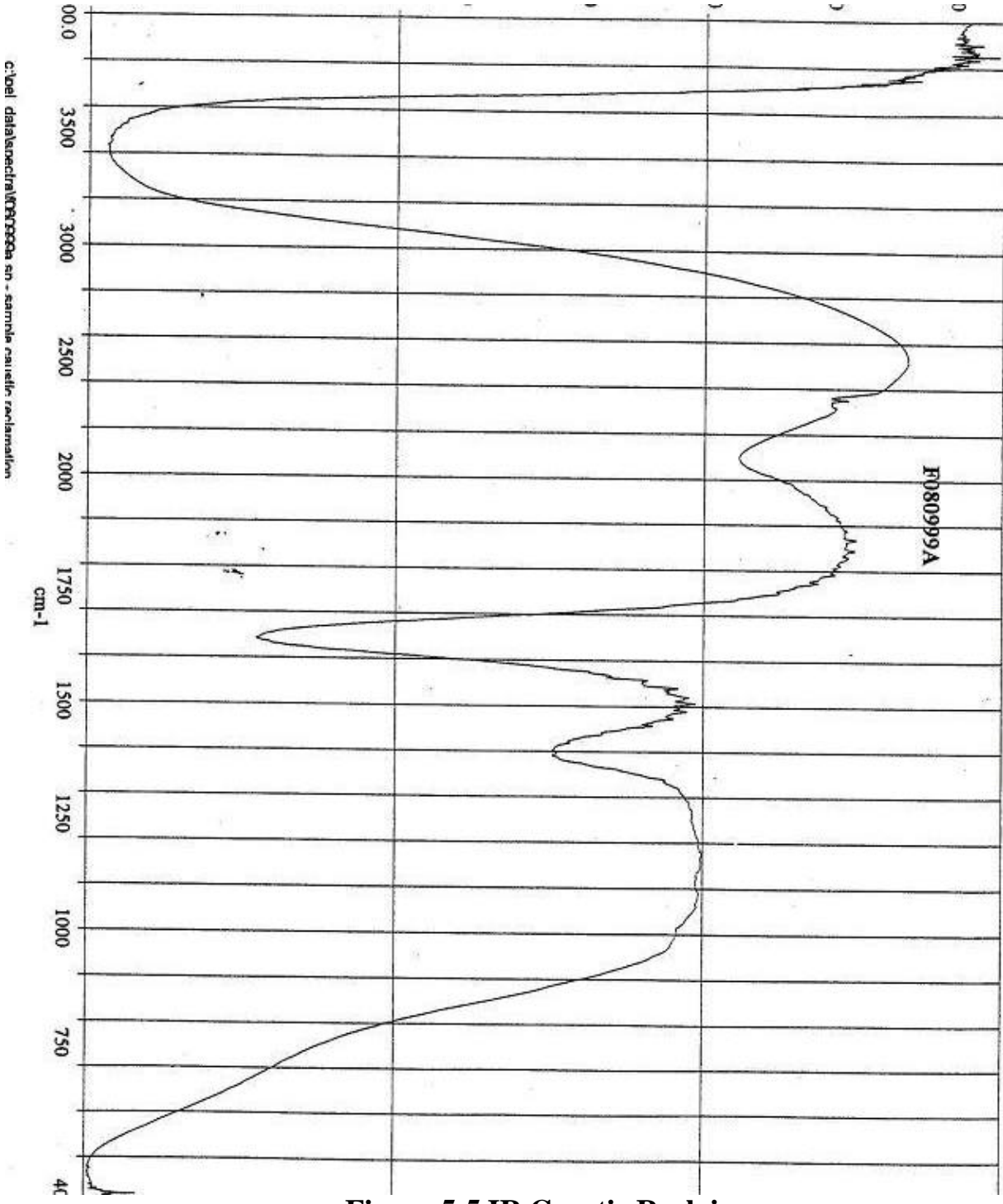


Figure 5.5 IR Caustic Reclaim

# SODIUM HYDROXIDE RECYCLING AND RECOVERY AT WATERVLJET ARSENAL

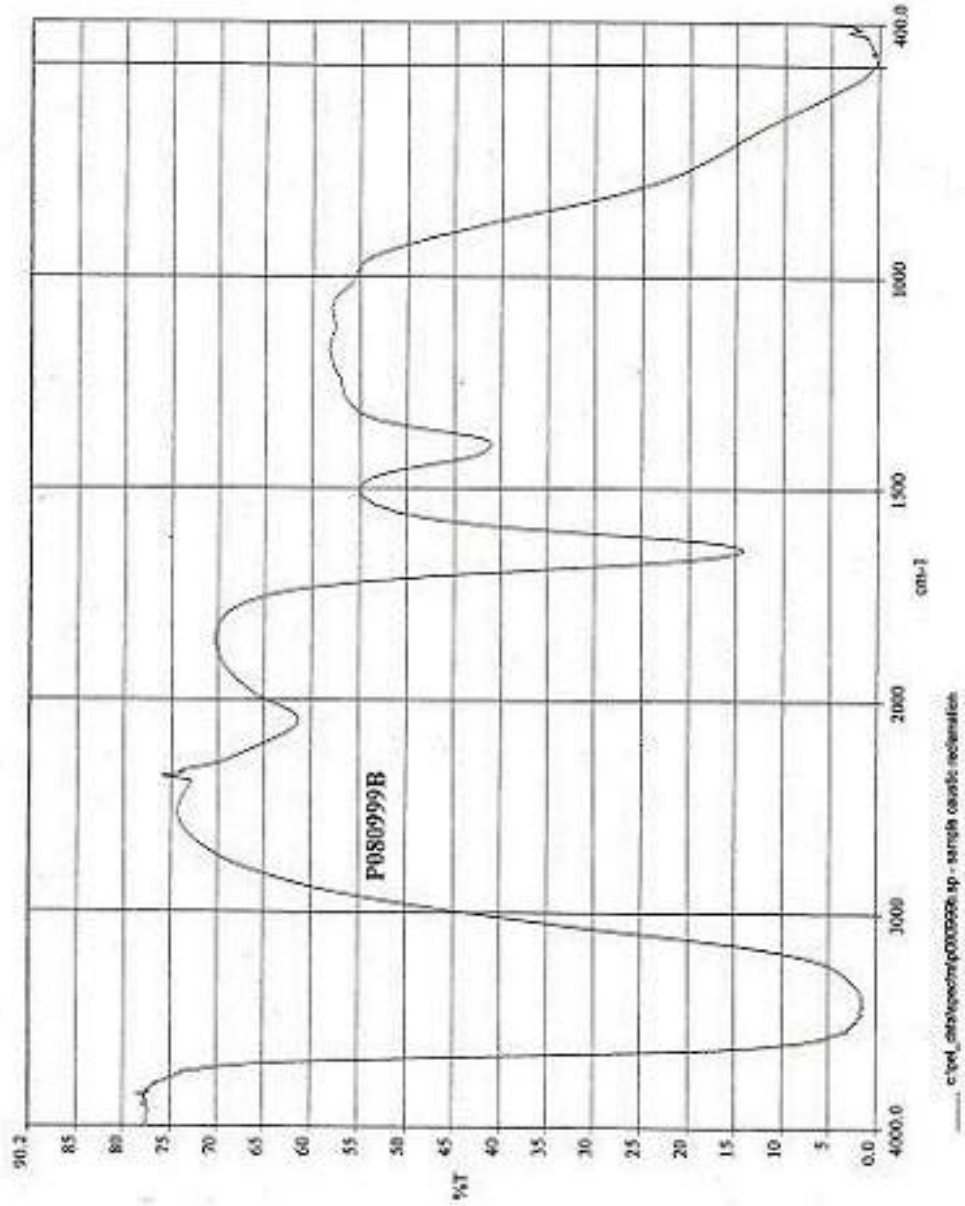


Figure 5.6 IR Permeate

# SODIUM HYDROXIDE RECYCLING AND RECOVERY AT WATERVLJET ARSENAL

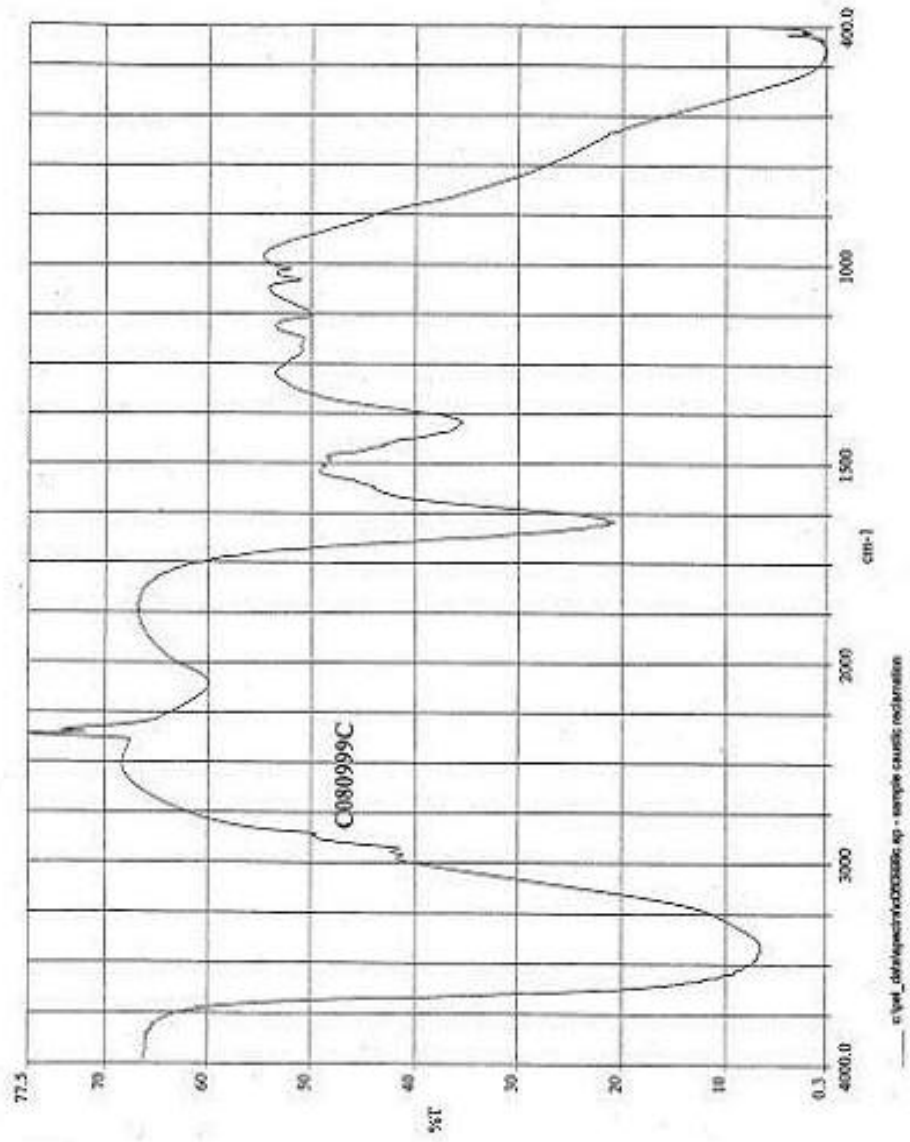


Figure 5.7 Concentrate Waste

# SODIUM HYDROXIDE RECYCLING AND RECOVERY AT WATERVLIET ARSENAL

## 6. Cost Assessment

### 6.1 Cost Performance

The V $\phi$ SEP technology was evaluated using the Environmental Cost Analysis Methodology (ECAM). This document is not enclosed but can be view as a separate document.

A comparison was made between the purchase and installation of a V $\phi$ SEP unit to recycle the caustic solution (Scenario 1) and the disposal of all caustic solution as hazardous waste (Base Scenario).

The V $\phi$ SEP unit from New Logic International Corp is mobile and can easily be moved from site to site. There are no site requirements except electrical power.

#### Pollution Prevention

	Scenario 1 VSEP	Base Scenario All Hazardous Waste
<b><u>Initial Investment Cost</u></b>		
Capital Equipment	72,000	0
<b><u>Annual Operating Cost</u></b>		
Direct Material	0	3,450
Labor	120,000	120,780
Utilities	14,237	14,146
Waste Management (Labor & material)	0	14,925
Regulatory Compliance	0	2,594
Training & Instruction	1,694	0
Medical Exams - Lost Labor	480	528
Medical Exams	200	220
Direct Material - membrane pack	5,000	0
Demobilization	0	0
	<b>\$141,611</b>	<b>156,643</b>

### 6.2 Cost Comparison to Conventional and Other Technology

A total economic analysis has been prepared evaluating the new technology of using the V $\phi$ SEP unit to recycle caustic solutions, Alternative Scenario 1, vs. the existing base scenario of totally disposing of the caustic solutions. The discounted payback for going with scenario 1, using the membrane system, is 5.34 years.

This P2/Finance, Pollution Prevention Financial Analysis and Cost Evaluation System, is a separate document. The project title is Caustic Recycle.

We have not found new technology that competes with the Vibratory Shear Enhanced Processing method especially the extended life of the membranes.

# **SODIUM HYDROXIDE RECYCLING AND RECOVERY AT WATERVLIET ARSENAL**

## **7.0 Regulatory Issues**

### **7.1 Approach to Regulatory Compliance and Acceptance**

The Watervliet Arsenal's Environmental Office was part of the team that brought the V $\diamond$ SEP technology here to reduce the waste streams generated by the cannon manufacturing process. They were constantly consulted through out every step of this project and witnessed the actual run of the unit. The New York State Department of Environmental Conservation has long been encouraging all industries to reduce waste steams and the Federal government has seconded this environmental push especially for Federal facilities.

## **8.0 Technology Implementation**

### **8.1 Department of Defense Requirements**

Large quantities of spent sodium hydroxide are produced by metal finishing facilities, both in private industry, DOD and DOE processes. Government facilities need to reduce the estimated 500,000 tons of sodium hydroxide they generate each year, which could result in at least a \$100 million savings each year. This new technology was also tried at Corpus Christi Army Depot with great success. They expressed a strong desire to institute this technology permanently at their metal finishing facility.

### **8.2 Transition**

The V $\diamond$ SEP system confirmed the ability of the technology to recycle caustic wash solutions. No further demonstrations are necessary. However, the V $\diamond$ SEP unit does not meet our requirement that it run with very little operator interface. This deficiency has been brought to the contractor's attention and is addressed in detail in the Lesson Learned section of this report. To date the contractor has not respond to this problem or addressed our concerns. We still feel this technology is worthy of other installation's need to reduce caustic waste streams. The V $\diamond$ SEP unit can be procured from New Logic International Inc. Emeryville, California for approximately \$70K and purchasers should especially read the Lessons Learned section of this report.

## **9. Lessons Learned**

Acceptance testing confirmed the ability of New Logic's V $\diamond$ SEP unit to recycle wash alkaline solutions. This means removing the oil, grease and dirt from the bath and leaving the good elements of the cleaning solution. However, a problem was encountered with the analytical testing of the solutions to verify this success. We used analytical methods per the Standard Method for Examination of Water and Wastewater to obtain values for pH, total solids, alkalinity and oil & grease. But we had great difficulty with the oil and grease analysis and so we used IR spectral analyses per ASTM E168 and ASTM D2357 to check for the surfactants to confirm that they were not being removed. IR spectral analyses is only qualitative and not quantitative.

## **SODIUM HYDROXIDE RECYCLING AND RECOVERY AT WATERVLIET ARSENAL**

During our attendance at a conference, we discovered a company, Armor Clean Division of Church and Dwight that had been working with membrane separations/recycling of aqueous cleaners for the past 5 years and had extensive expertise in analysis of these solutions. We had several talks with Armor Clean about our project and our shortcomings with testing and their projects and testing. We talked with them about developing a CRADA to share information and work on new testing methods, they at first seemed interested but finally decided not to enter into an agreement. Maybe they felt their research was worth more on the open market.

Due to this failure to establish an agreement, we did a literature search and came up with some interesting ASTM specifications:

G-120 Determination of Soluble Residual Contamination in Material and Components by Soxhlet Material, G-121 Preparation of Contaminated Test Coupons for the Evaluation of Cleaning Agents and G-122 Evaluating the Effectiveness of Cleaning Agents that with some modification we feel will result in easier and more accurate methods thus resulting in better data. Reference the email (pgs 37 & 38) from Max Phelps, PNNL team member, on his thoughts on these testing method. We unfortunately did not have the time or funding to more thoroughly investigate and try these methods.

# **SODIUM HYDROXIDE RECYCLING AND RECOVERY AT WATERVLIET ARSENAL**

## **10.0 Final Comments, Recommendations and Conclusions for Caustic and Solvent Recycle Using Vibratory Shear Enhanced Processing (VSEP)**

The prototypical VSEP based system that was assembled by New Logic International for caustics and solvents recycle has been deemed unacceptable for general use in Government Metal Finishing Facilities.

There were three criteria by which the VSEP based recycle process was evaluated in accordance with standards established under the intent of the ESTCP program for certifying proposed technologies.

1. Proposed system must be able to effectively and efficiently recycle caustic and solvent solutions without plugging and/or requiring active operator interfacing to prevent plugging or failure.
2. Proposed system must be relatively simple to operate such that a minimal of training is required for use.
3. Proposed system must be safe to both the environment and to personnel.

The VSEP system failed the second of these criteria.

While the VSEP technology shows considerable promise for recycling and extending the bath life potential for highly caustic solutions, the operator interfaces and controls required to safely use the equipment are too sophisticated and time consuming for general use by relatively untrained individuals.

Our testing has shown that the system cannot be left unattended for extended lengths of time without experiencing serious disruption either in the system itself or to the operation being performed. Specific problems with operations and controls are listed below.

### **10.1 Concentrate Valve Control Issues:**

The primary objectives for using membrane based technology to recycle caustic and solvent solutions are to substantially reduce the amount of waste produced by normal cleaning and plating operations, and to extend the bath life of the cleaning and stripping tanks being used.

The system being used to recycle these solutions and concentrate the waste product are operated in a batch-type fashion such that recycle operations are intended to be accomplished over a period of a few days. As such, the fraction of contaminant in the bath being recycled diminishes with time, and any control scheme for setting the consistency of the concentrate must be able to successfully match elimination of the concentrated waste with this reduction of waste content in the inlet flow.

## **SODIUM HYDROXIDE RECYCLING AND RECOVERY AT WATERVLIET ARSENAL**

The VSEP system offers two sets of methodologies for control of reject product elimination and concentrate adjustment. Both methodologies are based on the fact that space between the membrane plates become loaded with reject material as a normal part of fluid flow through the system. The reject material, or the material that does not flow through the membrane, collects until a signal is received to open the concentrate valve and force the reject material out of the system via the pressure provided by the inflow pump. Ideally, control of this concentrate valve should produce a highly concentrated product that contains little or no excess waste.

The first control method is by setting the duration between openings of the concentrate flow valve. The second is based on the percent load on the Torsion Bar that produces the vibratory shear on the membrane pack.

Duration based opening of the concentrate valve proved unacceptable because any effort to set the consistency of the reject product would require a time duration change between concentrate un-loadings due to the reduction of reject material being fed to the filter pack while the bath is being cleaned. Constant inflow of a gradually reduced fraction of waste material in that inflow should result in longer durations between unloading cycles. Attempts to use this method of control required fairly frequent adjustments by the operator between cycles to re-adjust the timing, and no reliable method for predicting timing intervals was found.

Percent loading is based on the premise that as the filter pack becomes loaded with reject materials, the percent load on the torsion bar increases. The operator can adjust the opening of the concentrate valve to coincide with a particular percent load setting, which should coincide with a relatively consistent loading of the filter pack. Percent load control proved unreliable however because of a general instability in the percent load readings on the torsion bar. Changes in the percent load readings were noted for relatively minor changes in temperature and humidity, as well as for extremely minor changes in vibration amplitude. Frequent operator intervention was required to maintain some consistency with regard to reject consistency and to avoid expelling inordinate amounts of excess, or dilute wastes.

The membrane pack will hold approximately 3-Liters of reject material before system plugging becomes a serious issue. Ideally, operation of the concentrate valve should result in a maximum of half (or 1.5-Liters) of the concentrated material to be expelled from the system. When more than 1.5-Liters of material is expelled, an excessive amount of unnecessary waste is produced. Samples taken during testing suggest that optimal performance can be achieved with concentrate un-loadings of 350-ml to 500-ml in size.

Adjusting the duration and extent of the concentrate valve opening can easily control the size of these un-loadings; however, the adjustment provided didn't give fine enough control.

# **SODIUM HYDROXIDE RECYCLING AND RECOVERY AT WATERVLIET ARSENAL**

## **10.2 System Startup Instability Issues:**

Because of the nature of the materials being recycled through the VSEP system, full time, unattended operation was not allowed. Therefore, the system had to be shut down whenever untrained operators were off shift. As such, the system would typically be restarted using the same control criteria that it was using when shut down.

On startup, the torsion bar and the percent load readings on that torsion bar are very unstable, making it impossible to avoid producing an excessive quantity of waste from the too frequent and unnecessary concentrate valve un-loadings resulting from this instability. Once the system becomes stable and steady state is achieved, the operator typically has to readjust the percent load control point and vibration amplitude control point until a fairly uniform level of concentrate consistency can be achieved again. For our operations, the control points used one day were not the same as the control points used on the following day. These differences were attributed to the temperature differentials observed for the facility that the VSEP system was being tested in, as well as minor differences between vibration amplitude settings. Ambient temperature in the facility being used could easily change as much 25°F within an hour or two of operation.

The problem was more severe as the duration of the shutdown increased such that a shutdown over a weekend resulted in much longer startup times than shutdowns that were only for a few hours.

Any efforts to flush the system, and avoid the startup problems, prior to these short-term shut downs were rapidly deemed unacceptable due to the excess amount of waste produced, thus defeating the purpose of having the system in the first place.

## **10.3 General System Instability Issues:**

The VSEP system was prone to developing instabilities in operation even after achieving what would normally be considered steady state operations. The rapid opening and closing of the concentrate control valve, which is air actuated and pneumatically controlled, caused the most common anomaly.

Every time the concentrate valve opened, pump pressure would rapidly drop and the percent load readings on the torsion bar would jump around the set point by as much as 6.0%. The pump would increase speed to make up for the loss of pressure, resulting in an immediate increase in the percent load reading due to the change in fluid flow. Quite frequently, the system would become unstable and continue dumping concentrate every two or three seconds as the system tried to stabilize.

Adjustments to the gain and reset values on the feed control and percent load valve control would stabilize the system once again; however, concentrate consistency would have to be readjusted to coincide with the differences in operating parameters. Given the right set of conditions, the system had the potential to once again become unstable with the new settings.

# SODIUM HYDROXIDE RECYCLING AND RECOVERY AT WATERVLIET ARSENAL

## 10.4 RECOMMENDATIONS

This system is recommended for general use in Government Metal Finishing Facilities given that the following changes are made to the prototype.

1. Eliminate all pneumatic controls and valves. Replace said controls and valves with electrical units. This recommendation is made for several reasons:
  - a. The air-actuated valves open and close too rapidly for the system to compensate, thus causing severe shock to the system and its components when under pressure. A pressure transducer was destroyed as a result of one of the air-actuated valves closing too rapidly and causing an overpressure in the line at the pressure transducer. The situation was relieved by forcing one of the air-actuated valves to remain open on shutdown.
  - b. System vibration and constant pressure shock causes airline connections to loosen and leak resulting in unstable performance and raising reliability issues.
  - c. The air lines are subject to condensation loading problems in hot and humid environments, which are typical of metal finishing facilities.
  - d. Clean and dry air is not readily available in these facilities. Use of a compressor is acceptable, but the constant cycling of the compressor motor proved to be irritating in the shop environments where testing was performed.
  
2. Provide concentrate valve control via permeate flow levels. This would eliminate any instability in the system due to changes in temperature or vibration amplitude.

While watching the system operate, we noticed an increase in permeate flow after every concentrate dump, and that the next concentrate dump typically occurred at approximately 82% of that flow level. The only parameter that offset this value was any change made to the inflow pump pressure.

Thus, a more efficient, or simpler, control scheme would be to register permeate flow at its maximum value for every dump cycle, and then open the concentrate valve when a reduction in flow to an adjustable set point, as a percentage of that maximum value, was reached. Work performed at Watervliet Arsenal suggests that this setting should be approximately 82% of the maximum-recorded value for any dump cycle, but this value would be dependent on the properties of the membranes being used, and the material flowing through the membranes. Properly executed, the control process would be able to compensate for changes made to the inflow pressure and for the temporary instability in permeate flow resulting from the opening and closing of the concentrate flow valve.

For example: On system startup, permeate flow would be registered at 10-seconds after initialization of vibration of the filter pack. Initial concentrate valve opening would default to open at 90% of that value to prevent inadvertent plugging of the filter pack.

## **SODIUM HYDROXIDE RECYCLING AND RECOVERY AT WATERVLIET ARSENAL**

After the concentrate valve opens and then closes, and after a 3-second delay to allow for system re-stabilization, the permeate flow would again be registered, and the concentrate valve set to open at a predetermined and adjustable set point.

If a change is made from the control panel to the inflow pressure, the permeate flow rate should be registered after a 5-second delay to allow for re-stabilization of the system, and the concentrate valve set to open at a predetermined and adjustable set point.

3. On start-up, the concentrate flow should be directed to the inflow for at least the first 10-minutes of operation. This would eliminate the need to constantly monitor system conditions during warm-up, and avoid the generation of unnecessary waste. This value should be adjustable with a default value of at least one-half hour.

One of the primary objectives for developing a more automated system was to minimize operator intervention and/or a need for specialized training. We found the VSEP system to be extremely unstable during start-up, regardless of whether the system was shut down for a few minutes, or a few days. The instability usually caused an excessive amount of very dilute waste to be discharged, thus defeating the purpose of using the equipment. Stabilizing the system usually required rapid changes of operating set points, which usually served to cause a total resetting of all operating parameters from any previous operations.

We found that system stabilization could be achieved fairly rapidly if the system were left to settle into a steady-state condition without operator intervention; however, an excessive amount of waste would be generated. The easiest way to circumvent this problem, without generating too much unnecessary waste, was accomplished by directing the concentrate flow to the inflow for the first few minutes of operation. This operation was performed without shutting off any normal inflow to the pump. Thus the operation actually served to help clean the membrane pack and enhance performance.

The flushing operation should be directed such that all lines in the system, as well as the membrane pack, are cleaned with fresh solvent. Current flushing of the system only cleans the inflow line, the pump, and the filter pack.

One of the objectives for making the system transportable was to render the machine useable for a variety of different solutions by merely changing out the filter pack and making some minor adjustments to operating parameters.

While the unit could meet these criteria given the changes I've outlined above, an incomplete flushing of all lines and internals to the machine would result in severe cross-contamination problems for the user.

Add a user-selectable option in the Alarms Page to disable or enable the pH and Temperature Indicator alarms. Oils and other materials in the baths being cleaned tend to interfere with the correct operation of the probes being used, resulting in system shutdown from faulty and inaccurate readings. The user should be able to enable the alarms if the probes are working

## **SODIUM HYDROXIDE RECYCLING AND RECOVERY AT WATERVLIET ARSENAL**

properly, and disable them if they are not. The intent of having the pH and Temperature probes are primarily for informational purposes.

**ALARMS:** The alarms work very well for shutting down the system in the event of feed line failure, and for membrane pack failure. There is no way to disable either set of alarms, and neither set of alarms should be able to be disabled by the user.

It was found to be advantageous to use the CIP tank to set concentrate consistency prior to directing flow to a waste drum. The CIP tank is fixed with a high-level switch and low-level switch. During our operations, the system became unstable and an excessive quantity of waste was produced which rapidly filled the CIP tank. The high level switch on the CIP Tank turned off the pump, but did not turn off the Vibratory Shear action to the membrane pack, or shut the inflow valve. The CIP tank flooded to the point of overflow by a siphoning effect that fed fluid to the CIP even though the pump was shut off.

When performing solvent addition, the Low-Level Switch halts the operation well before the CIP tank is emptied. To circumvent the problem, the operator must either physically hold the switch in the open position, or manually drain the tank. Both operations are deemed unsatisfactory from a safety standpoint.

It is recommended that the High-Level Switch on the CIP tank be set to completely shut down the system, and that the Low-Level Switch be disabled.

A technique by which the system can determine whether or not the bolts holding the membrane pack together are intact or not needs to be designed and incorporated into the system. During one of our experimental runs, three of these bolts sheared while the system was left unattended. The shearing of those bolts caused the system to become unstable with respect to percent load on the torsion bar, and an excessive quantity of dilute waste was generated.

One solution may be to set the high alarm point on the percent load reading to some preset value that would reflect any shearing of the bolts, but we are not sure if this would provide a reliable and repeatable shutting down of the system in event of failure.

While the newly designed, pre-assembled filter packs provided a eased change-out, we would still recommend that a completely enclosed pack be designed for use in the future.

Vibration amplitude is difficult to monitor given that the sticker that attaches to the membrane pack is difficult to see in low-light conditions. We would recommend a small piece of sheet metal be designed such that it can be attached to the front-most bolt on the filter pack. This piece of sheet metal should have the pattern set with a high-contrast color scheme that can easily be seen in even low-light conditions. An additional, and highly desirable option would be to place a small lamp inside the system in such a manner as to make the amplitude indicator visible.

# **SODIUM HYDROXIDE RECYCLING AND RECOVERY AT WATERVLIET ARSENAL**

## **10.5 CONCLUSIONS**

VSEP technology was found to be highly effective for recycling high pH solvents and baths of the type typically found in metal finishing operations. The membranes did not become plugged, nor were they prone to failure. The system is relatively easy to set up, and with a few minor changes in the operator interface, can be made extremely easy to use.

Current system requires an in-depth understanding of the system and its components in order to set up and operate given the current control schemes. A simplification of the interface, along with the improved control scheme outlined above, should make the system useable by virtually any qualified operator throughout the DoD sector. Qualifying should be able to be accomplished in a matter of minutes, and not require an in-depth understanding of what the system is doing, or how it is doing it.

The system can be easily automated to the point where an operator can set the appropriate valves, turn the system on, adjust the amplitude, and walk away, given that a few cursory adjustments need to be made to the system to maximize performance over the course of the first few hours. Our work has shown that if the above changes are made, the unit can be easily shut down during off-shift, and then restarted again by simply hitting the respective Off and On buttons, once the system has been adjusted to maximize efficiencies.

Long-term use of this technology will prove to be cost effective, safe, and reliable given the changes outlined in the RECOMMENDATIONS section 10.4 are implemented.

# SODIUM HYDROXIDE RECYCLING AND RECOVERY AT WATERVLIET ARSENAL

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