Safer Alternatives for the Chemical, Pharmaceutical and Biotechnology Industries: Process Hose Cleaning

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EXECUTIVE SUMMARY

It is estimated that there are more than 1,200 chemical manufacturing facilities in California. Various types of solvents are used extensively to clean reactor tanks and associated equipment employed by chemical, pharmaceutical and biotechnology manufacturers. Companies with batch and campaign operations particularly rely on solvent cleaning operations when they are changing products that require different input chemicals. Many of the solvents that are used for cleaning are classified as Volatile Organic Compounds (VOCs) which contribute to photochemical smog. Some of the solvents pose toxicity problems and they expose workers and community members. Use of the solvents results in air emissions and the generation of large amounts of hazardous waste.

This project focused on identifying and analyzing options for reducing or eliminating the use of solvents used in typical cleaning operations for reactor tanks and other related equipment like valves and process hoses. The project was sponsored by U.S. EPA Region IX and Cal/EPA's Department of Toxic Substances Control (DTSC). The project was conducted by the Institute for Research and Technical Assistance (IRTA), a small nonprofit technical environmental organization with specific expertise in solvent alternatives. IRTA analyzed and compared the costs of options for reducing or eliminating the use of solvents in process hose cleaning for hypothetical large and small operations. These process hoses are used to transfer intermediates or products to and from reactors during manufacturing.

IRTA analyzed the cost of adopting options for reducing or eliminating the use of a mix of Halogenated and non-halogenated solvents used for cleaning process hoses in a hypothetical chemical, pharmaceutical or biotechnology manufacturing plant. Two sizes of operations, a small operation where 10 hoses per day are cleaned and a large operation where 20 hoses per day are cleaned, were considered. The six options for reducing solvent use included using acetone exclusively, eliminating one of the solvent hose flushing operations, using a lower volume of solvent for the flushing operation, sending the spent acetone off-site for reuse or reutilization by another company, sending the spent acetone off-site for recycling and recycling the spent acetone on-site for reuse in the process. The reason for focusing on acetone as the exclusively used solvent is that acetone is not classified as a VOC and is lower in toxicity than nearly all other organic solvents. In California, in particular, where VOC and toxic solvents are heavily regulated, acetone offers a particular advantage.

The four options for eliminating solvent use included converting to one of two alternative water-based cleaners in a high or low volume flushing operation. In another project, IRTA worked with a pharmaceutical company to conduct screening tests of low-VOC, low toxicity alternatives to traditional solvents used today by many companies (Wolf, 2011). Two of the best performing alternatives were the water-based cleaners analyzed here.

Table E-1 summarizes and compares the annualized cost of adopting options for reducing or eliminating the use of solvents in the small hose cleaning operation. The costs of adopting the options in the large hose cleaning operation are similar. The values show that the lowest cost options are to convert from solvents to one of the water-based cleaners even if a high flushing volume is required. Although scaled-up testing of the water-based cleaners was not conducted, the results of IRTA's cost analysis demonstrate that the option is worth pursuing. The cost of using a water-based cleaner, assuming it performs well in the scaled-up tests, is much lower than the cost of using a mixed stream of solvents for cleaning or the cost of using acetone exclusively in the operation. The other options that are relatively

low cost are to use a lower volume of solvent for flushing and to recycle the solvent used in the hose cleaning operation on-site.

Table E-1 Annualized Cost Comparison of Options for Reducing or Eliminating Solvent Use in Small Hose Cleaning Operation			
	Annualized Cost		
Mixed Halongenated and Non-Halogenated Solvent Use	\$1,571,079		
Exclusive Use of Acetone, High Volume Flushing	\$1,266,760		
Eliminate One Flush	\$633,380		
Lower Volume Flushing	\$253,352		
Reutilize Acetone	\$1,085,293		
Recycle Acetone Off-Site	\$1,104,598		
Recycle Acetone On-Site	\$289,035		
Convert to CIP 100/ProKlenz Water-Based Cleaner, High Volume Flushing	\$55,078		
Convert to CIP 100/ProKlenz Water-Based Cleaner, Low Volume Flushing	\$22,032		
Convert to Metalnox M6321 Water-Based Cleaner, High Volume Flushing	\$87,980		
Convert to Metalnox M6321 Water-Based Cleaner, Low Volume Flushing	\$35,193		

The results presented here should be useful to many chemical, pharmaceutical and biotechnology companies in California and the U.S. as a whole. The approach provides a framework for evaluating and selecting the best options for any company's specific operations.

TABLE OF CONTENTS

Disclaimer	
Acknowledgements	ii
Executive Summary	ii
Table of Contents	ν
List of Tables	vi
List of Figures	vii
I. Introduction and Background	1
II. Process Hose Cleaning Operations	3
Hose Cleaning Description	4
Cleaning Solvents	4
Case Study Operations	5
Approach to Cost Analysis	5
Options for Reducing Solvent Use	6
Keep Solvents Segregated	
Convert to Acetone Exclusively in Precleaning Step	8
Change Order of Operations and Eliminate One Solvent Flush	9
Reduce Use of Acetone in Flushing Operations	
Reutilize Acetone	10
Recycle Acetone Off-Site	
Purchase and Use On-Site Still	
Comparison of Options for Reducing Solvent Use	16
Options for Eliminating Solvent Use	
Conversion to CIP 100/ProKlenz	
Conversion to Metalnox M6321	
Comparison of Conversion Options to Baseline Case	22
Uncertainties in the Cost Analysis	22
III. Results and Conclusions	24
IV Pafarancas	26

LIST OF TABLES

Table E-1. Annualized Cost Comparison of Options for Reducing or Eliminating Solvent Use in Small Process Hose Cleaning Operation	iv
Table 2-1. Solvent Use and Waste Generation for Case Study Operations	5
Table 2-2. Cost of Disposal for Mixed Halogenated and Separated Waste Streams	8
Table 2-3. Comparison of Annual Cost of Hose Cleaning Operations—Using Mixed Solvents and Using Acetone Exclusively	9
Table 2-4. Comparison of Annual Cost of Hose Cleaning Operations—Using Mixed Solvents, Using Acetone Exclusively and Eliminating One Flush	10
Table 2-5. Comparison of Annual Cost of Hose Cleaning Operations—Using Mixed Solvents, Using Acetone Exclusively, Eliminating One Flush and Reducing Acetone Use	11
Table 2-6. Annual Disposal Cost for All Options and Credit for Reutilization	12
Table 2-7. Annual Disposal Cost for All Options and Credit for Reutilization and Recycling	12
Table 2-8. Annualized Cost Comparison for Use of On-Site Distillation System	16
Table 2-9. Annual Savings Compared With Baseline Option of Using Acetone Exclusively	16
Table 2-10. Use of CIP 100/ProKlenz Detergent in Hose Flushing Operation	18
Table 2-11. Annual Cost Comparison for CIP 100/ProKlenz Cleaning Agent Assuming Off-Site Disposal	20
Table 2-12. Annual Cost Comparison for CIP 100/ProKlenz Cleaning Agent Assuming On-Site Treatment	20
Table 2-13. Annual Cost Comparison for Metalnox M6321 Cleaning Agent Assuming Off-Site Disposal	21
Table 2-14. Annual Cost Comparison for Metalnox M6321 Cleaning Agent Assuming On-Site Treatment	21
Table 2-15. Annualized Cost Comparison of Solvent Baseline and Water-Based Cleaning Option With High Volume Flushing	22
Table 3-1. Annualized Cost Comparison of Options for Reducing or Eliminating Solvent Use	24

LIST OF FIGURES

Figure 3-1.	Typical Process Hose	}
Figure 3-2.	Typical Distillation System14	ļ

I. INTRODUCTION AND BACKGROUND

Californians are strongly concerned about the quality of their environment and are vitally interested in minimizing the releases and generation of toxic and other hazardous materials. In response to continuing concerns about pollution, in 1998, the Legislature augmented the State's Pollution Prevention (P2) Program at California's Environmental Protection Agency Department of Toxic Substances Control (DTSC) through legislation called Senate Bill 1916. The program involves selecting certain industries every few years for detailed focus to address P2 priorities and promote implementation of source reduction measures. For the fiscal year 07/08 cycle of SB 1916, DTSC selected the Chemical Industry. The Chemical Industry project is a voluntary program that addresses an industry primarily composed of large businesses but many members of the industry are also small and medium sized businesses. DTSC has established a partnership with the Chemical Industry Council of California (CICC) as part of the project which is designed to reduce hazardous waste generation and other multimedia releases.

According to the American Chemistry Council, the California chemical industry produces about \$27 billion worth of goods and contributes nearly \$17 billion to the gross state product. In 2004, the most recent year for which data are available, there were 1,206 chemical manufacturing facilities in the State with 90,970 employees. This industry includes a wide variety of manufacturing operations used to produce inorganic chemicals, organic chemicals, plastics and synthetic resins, drugs, soap, detergent and cleaning preparations, paints, varnishes, lacquers, enamels and agricultural chemicals. The chemical industry ranks first in hazardous waste generation and fifth in total hazardous releases in the federal Toxics Release Inventory (TRI) among all California industries. The highest concentrations of TRI releases are in southern California, especially in Los Angeles, Orange and Riverside counties, and around the Bay Area and the northern Central Valley. The industry's air emissions account for 95 percent of the industry's total on-site disposal and other releases and 75 percent of the industry's total on- and off-site releases.

According to DTSC manifest data, the chemical industry generated about 70,000 tons of hazardous wastes in 2005. Major waste generating processes in the chemical industry include cleaning activities like washing out reactor vessels and other production equipment, bottles, glassware, containers and tanks and flushing lines, valves and hoses. Waste streams classified as oxygenated, hydrocarbon and unspecified solvents account for 17 percent of major waste stream generation and inorganic aqueous solutions also account for 17 percent. The spent solvents and aqueous streams include materials used in cleaning activities. The California Air Resources Board (CARB) reports that the chemical industry was responsible for 4.6 million pounds of toxic air emissions in 2002. Many of the chemicals that comprise these toxic air emissions are solvents of various types and it is likely they are used for cleaning activities. Most of the solvents used for cleaning are classified as Volatile Organic Compounds (VOCs) which contribute to photochemical smog and many are considered toxic as well.

The focus of this project was to identify, evaluate and analyze alternative safer methods of cleaning reactor tanks and related equipment for the chemical industry. The aim of the project was to reduce or eliminate the use of toxic and VOC cleaning materials and minimize the generation of hazardous waste and air emissions. Use of safer cleaning alternatives protects workers and community members in California. The Institute for Research and Technical Assistance (IRTA) is a nonprofit organization established in 1989. IRTA's mission is to identify, develop, test and demonstrate safer alternatives in a

variety of applications. A significant focus of IRTA's work has been on solvent alternatives. IRTA partnered with DTSC's Pollution Prevention group to conduct the project which was sponsored under EPA's Pollution Prevention Grants Program.

In the original project formulation, IRTA and DTSC wanted to focus on methods of reducing or eliminating the use of solvents in a commonly used operation that involved cleaning reactor tanks or associated equipment in the chemical industry. The best candidates for the project are the types of operations employed by companies that make many different products in batches. In a batch process, a specific substance or intermediate is manufactured in a so-called campaign for a period ranging from a few days to months until a sufficient amount of substance is produced to satisfy the contract. At the end of the campaign, another substance is made and the same equipment with different configurations is often used. Different raw materials are used as inputs, different process steps may be involved and different waste streams may be generated. Because they are producing or blending these different products in shorter runs, their cleaning needs between product runs are greater and they use a number of solvents and high volumes of solvents for cleaning.

Since all companies in the chemical industry and particularly pharmaceutical and biotechnology companies with batch operations need to conduct process hose cleaning, IRTA focused on this end use for evaluation in this report. In Section II of this document, IRTA presents a detailed case study analysis of hose cleaning for two sizes of operations, large and small, for hypothetical companies. The evaluation involves devising methods of reducing the amount of solvent used for these operations and reducing the cost of using the cleaning solvent. It also includes analysis of substituting water-based cleaners for solvents used in the hose cleaning operation. Finally, Section III of the document summarizes the results of the analysis.

II. PROCESS HOSE CLEANING

Many pharmaceutical, biotechnology and chemical companies use braided stainless steel, teflon lined process hoses for transferring products and intermediates to and from reactors. A picture of a typical hose of this type is shown in Figure 2-1. Companies that make custom batch products of various kinds change the reactants, intermediates and products often. As a result, each time the product mix changes, the company needs to perform product-to-product cleaning. Many components of the system require cleaning; specifically, this project focuses on the process hoses. Pharmaceutical and biotechnology companies, in particular, must meet stringent FDA standards so cleaning the hoses effectively between runs of products to maintain product quality is an ongoing challenge.



Figure 2-1. Typical Process Hose

In general, companies use a range of different solvents to accomplish the cleaning. Solvents commonly used for process hose cleaning may include methylene chloride, N-methyl pyrrolidone (NMP), methanol and acetone. Methylene chloride, a chlorinated solvent, is a listed hazardous waste under the Resource Conservation and Recovery Act (RCRA). It is a carcinogen and is on California's Toxic Air Contaminant (TAC) list, EPA's Hazardous Air Pollutant (HAP) list and is listed on Proposition 65. It is exempt from VOC regulations and is not considered a VOC. An MSDS for methylene chloride is shown in the Appendix. NMP is a reproductive and developmental toxin and is listed on Proposition 65. The chemical is classified as a VOC. An MSDS for NMP is included in the Appendix. Methanol is also classified as a VOC, is a listed HAP and a listed RCRA hazardous waste. An MSDS for the chemical is shown in the Appendix. Acetone is exempt from VOC regulations and is lower in toxicity than most other organic solvents. It is a listed RCRA hazardous waste. An MSDS for acetone is shown in the Appendix.

Reactors and the associated equipment like valves and hoses are often cleaned in place between operations or steps in operations. This approach is a good method of cleaning the hoses that carry the products and intermediates to and from the reactor. In many cases, however, this approach may not ensure the cleanliness of the hoses, so often the process hoses are removed from the system and cleaned in a central location.

This section focuses on centralized process hose cleaning operations in two hypothetical pharmaceutical, biotechnology or chemical plants that routinely have batch and campaign operations, a large hose cleaning operation and a small hose cleaning operation. IRTA analyzed methods of reducing the use of traditional solvents and reducing the cost of the cleaning operations. Although scaled-up testing to identify suitable safer alternatives would be a better approach over the long term, shorter term options, until the alternatives testing could be conducted, can be implemented in the meantime. Based on alternatives that have performed well in screening tests in related work (Wolf, 2011), IRTA also analyzed the cost of adopting two water-based cleaners for the large and small hypothetical hose cleaning operations.

HOSE CLEANING DESCRIPTION

Hoses can be cleaned in place on the reactors and other equipment or they can be taken to a central location for cleaning. This analysis addresses a separate hose cleaning station in a central location. Companies use the same general procedures for cleaning hoses at a station. First, there is a precleaning step where the hose is cleaned with a solvent which may vary depending on the company and the types of operations they have. Second, in the process water cleaning step, the hoses are cleaned with water which would generally be deionized water. Third, in the second solvent cleaning step, the hoses are cleaned with a solvent, commonly the same solvent for all hoses. Fourth, in the drying step, the hoses are dried with nitrogen. Fifth, in the inspection step, the hoses may be wiped with solvent and visually inspected for contamination.

In general, for the first step, a pre-cleaning solvent that is effective in solubilizing the product is the solvent of choice. The second step, the water flush, is designed to remove any water soluble contaminants in the hose that the pre-cleaning solvent may not have removed. In the third step, a solvent is used as a final clean and to help with drying the water; in effect, the solvent displaces the water in the hose. The nitrogen is used to completely dry the hose, removing any traces of solvent or water that could remain.

For the pre-cleaning step, the hose is attached to the solvent source which may be a drum or a tank containing the solvent. The other end of the hose is attached to a waste drum or tank. The solvent is pumped through the internal diameter of the hose for a flushing action. For the process water cleaning step, one end of the hose is connected to the source of the process water and the other end is connected to a waste drum or tank. In this case, water flushes through the hose diameter. For the solvent cleaning step, the procedure is the same as that used for the pre-cleaning step. It may involve use of a different solvent. For the drying step, one end of the hose is connected to the nitrogen source. The other end is connected to the waste tank. The nitrogen can be released to the atmosphere.

CLEANING SOLVENTS

In California, a variety of different local air districts regulate stationary sources like pharmaceutical or biotechnology manufacturers and chemical companies. There are many regulations that focus on VOC sources because of the high ozone concentrations in the atmosphere in some air district jurisdictions. As a result, there is pressure on manufacturers to adopt solvents that are not classified as VOCs. Some air districts also have stringent regulations that affect the use of solvents on the TAC list like methylene chloride. From an overall health and environmental standpoint, therefore, many companies may use a variety of solvents like those listed above, but much of the solvent cleaning is likely to be done using acetone. The solvent is fairly aggressive for organic contaminants like many of those that would be encountered in a hose cleaning operations; it is not a VOC and is not on any toxics lists.

For both the large and small volume hose cleaning operations, it was assumed that the pre-cleaning step is performed with a variety of solvents, including NMP, methanol, methylene chloride and acetone. It was further assumed, because of California regulations, that acetone is used exclusively for the second solvent cleaning step.

CASE STUDY OPERATIONS

The analysis was performed for two sizes of operations, a small operation and a large operation. In the small operation, a technician cleans 10 hoses per day and, in the large operation, 20 hoses are cleaned per day. For each hose, 25 gallons of solvent are used in the pre-cleaning step, 25 gallons of water are used in the process water cleaning step and 25 gallons of solvent are used in the solvent cleaning step. In both the large and small operation, on an annual basis, one-fourth of the hoses are pre-cleaned in the first step with each of the four solvents, NMP, methanol, methylene chloride and acetone. In all cases, because of the emphasis on using low VOC materials, all hoses in both operations are cleaned in the third step with acetone.

Pharmaceutical, biotechnology and chemical companies, because of their stringent cleaning requirements, generally use solvent in a one pass through system. What this means is that they use the solvent once for cleaning and dispose of it as hazardous waste. Accordingly, the spent solvents, once they have been used, are routed to a consolidated solvent stream which is picked up periodically by a hazardous waste hauler for disposal.

For purposes of analysis, it was assumed that in both operations, a technician cleans the hoses five days per week, 52 weeks per year. On this basis, Table 2-1 summarizes the amount of each solvent used in the cleaning operation and the amount of each waste solvent generated in the process. It was assumed that little solvent is lost in the process because it is used in closed flushing operations and very little evaporation is likely to occur. For both operations, emissions of solvent were assumed to be no more than 10 percent of the solvent used. This emissions estimate is likely to be higher than the emissions from many hose cleaning operations and this was intended to represent a maximum value so the baseline disposal costs would be conservative. Thus, 90 percent of the solvent used in the flushing operation will require disposal as hazardous waste.

Table 2-1 Solvent Use and Waste Generation for Case Study Operations					
	Small Operation Large Operation				
Number of Hoses Cleaned/Year	2,600	5,200			
Solvent Use (gallons/year)	2,600	5,200			
Methylene Chloride	16,250	32,500			
Methanol	16,250	32,500			
NMP	16,250	32,500			
Acetone	81,250	162,500			
Solvent Waste (gallons/year)					
Methylene Chloride	14,625	29,250			
Methanol	14,625	29,250			
NMP	14,625	29,250			
Acetone	73,125	146,250			

APPROACH TO COST ANALYSIS

IRTA analyzed and compared the cost of several different options for reducing or eliminating the use of solvents in the hypothetical small and large hose cleaning operations. In all cases, annual costs were determined for the options. In certain cases, it would be necessary to purchase capital equipment and

in such cases, the costs were annualized so they could be added to the annual costs for other cost components. To be conservative, in annualizing the cost, IRTA assumed a cost of capital of 4% for the equipment which is likely to be higher than the actual cost of capital presently. IRTA also used a conservative estimate of the timeframe which represented the average life of the equipment for amortizing the cost. In all cases, the basis for the costs that are used is discussed. This transparency establishes a framework so users could analyze costs in the same manner for a specific situation that requires different assumptions.

The analysis presented here focused on determining the cost components that would change if a user adopted a particular option. There was no attempt to analyze all of the costs associated with the operation. As an example, the energy costs of an option were only calculated and presented if adopting the option would lead to a change in energy use; the labor costs were only calculated if adopting the option would lead to a new requirement for labor. Using this strategy means that the same cost components were not evaluated for every option.

OPTIONS FOR REDUCING SOLVENT USE

Seven options for reducing the use of solvent and eliminating some of the solvents in the hose cleaning operation were examined. The first option is to keep the solvents separated rather than combining them in a mixed waste solvent stream. The second option is to convert all cleaning operations to acetone exclusively and eliminate the use of the other solvents. The third option is to modify the operations by changing the order of the water and solvent cleaning steps and eliminating one of the solvent cleaning steps. The fourth option is to reduce the use of acetone in the cleaning operation. The fifth option is to sell the spent acetone for reutilization. The sixth option is to send the acetone off-site for recycling. The seventh option is to purchase a still for recycling the acetone on-site. Each of these options is considered in more detail below for the small and large hose cleaning operations.

Keep Solvents Segregated

It is often beneficial from a cost standpoint to keep waste streams separate. In particular, chlorinated solvents, like methylene chloride in this case, are more expensive to dispose of because they contain halogens which have low heating or BTU value. Before they can be burned, the BTU value must be enhanced so disposal is more expensive. According to one disposal company, for waste streams with less than 3% halogens, the cost of disposal from a bulk tank of spent solvent is about 11 cents per pound (PSC, 2011). The cost of disposal from a bulk tank of spent solvent is about 25 cents per pound for waste streams with more than 3% halogens. Referring to Table 3-1 above, the amount of waste requiring disposal for the small hose cleaning operation is 117,000 gallons of solvent per year. Based on the values of waste for the individual solvents, methylene chloride accounts for 12.5% of the stream. The chlorine content (by weight) in the methylene chloride is about 84%. The composition of the stream would exceed 3% halogens if the streams were combined. The same reasoning holds true for the large hose cleaning operation in the table.

The cleaning technician currently connects one end of the hose for the flushing operation to the solvent source (a drum or tank of new solvent) and the other end of the hose to the waste solvent tank. To keep the individual solvent streams separate, the technician would have to vary the procedure. In cases where methylene chloride was used for the flush, instead of connecting the other end of the hose to the solvent waste tank, the hose would have to be connected to individual empty drums, preferably the drums that delivered the methylene chloride virgin solvent. For all other solvents that are used, since

they contain no halogens, and for the second flushing operation with acetone, the hose could still be connected to the currently used waste tank since this tank would contain only acetone and other non-halogenated spent solvents.

Each hose flush generates about 22.5 gallons of waste solvent, assuming the 10 percent evaporation value. This means that one 55-gallon drum could be used for two solvent flushes for the methylene chloride used in the first flush. The metering system could be adjusted to ensure that each drum of methylene chloride waste solvent was filled with 55 gallons before another drum would be required. The company could use the drums that held the virgin solvent used in the operation to hold the spent solvent so there would be no additional cost to do this. If this were too complex to handle, the company could use totes which hold 275 gallons of material. The waste hauler would supply totes to the company at a cost of \$150 each (PSC, 2011). Assuming the company would have to use the waste hauler totes for the methylene chloride spent solvent stream, the small operation would require 54 totes per year to hold the waste solvents. The large operation would require 107 totes. The cost of securing these totes would amount to \$8,100 per year for the small operation and \$16,050 for the large operation.

The small operation generates 102,375 gallons of spent non-halogenated solvent annually and 14,625 gallons of halogenated solvent per year. The large operation generates 204,750 gallons of non-halogenated spent solvent per year and 29,250 gallons of spent halogenated solvent per year. Because they generate such a large amount of waste solvent, these companies would have bulk tanks for disposal of the spent solvents. The waste hauler would use a vacuum truck to transfer the waste from the bulk storage tank to the truck for disposal. For the spent methylene chloride, in the case of the separated stream, the waste hauler would use the truck to transfer the solvent from the totes to the truck. The cost of disposal for the spent non-halogenated solvent stream would amount to 11 cents per pound based on an average density of about seven pounds per gallon. The cost for disposal for the spent methylene chloride stream would be 25 cents per pound based on a density of 11 pounds per gallon. The cost for disposal of the combined stream would be 25 cents per pound based on a density of 7.5 pounds per gallon.

On this basis, the cost of disposal for all of the spent solvents, assuming the streams are combined is \$219,375 annually for the small operation and \$438,750 annually for the large operation. The cost for disposal of a separated stream is lower. In this case, the cost of disposal for the small operation would amount to \$119,048. Assuming the streams are kept separate, the cost of disposal for the large operation would be \$238,095.

Table 2-2 compares the cost of disposal for the small and large operations for the case where the waste streams of the halogenated and non-halogenated solvents are combined and the case where the waste streams are kept separate. The cost of obtaining totes from the waste disposal company is included for the case where the streams are separated.

The values of Table 2-2 demonstrate that the cost for disposal of the mixed stream is much higher than the cost of keeping the halogenated and non-halogenated solvents separate even when the company has to purchase totes from the waste hauler. For both the small and the large operations, the cost of disposal of the separated streams is about 42% lower than the cost of disposal of the mixed streams. The savings for the small and large operations respectively are about \$92,000 and \$185,000 annually.

Table 2-2 Cost of Disposal for Mixed Halogenated and Separated Waste Streams				
	Mixed Halogenated Stream	Separated Stream		
Small Operation				
Waste Volume (gallons/year)	117,000	117,000		
Disposal Cost (per year)	\$219,375	\$119,048		
Tote Cost (per year)	-	\$8,100		
Total Cost (per year)	\$219,375	\$127,148		
Large Operation				
Waste Volume (gallons/year)	234,000	234,000		
Disposal Cost (per year)	\$438,750	\$238,095		
Tote Cost (per year)	-	\$16,050		
Total Cost (per year)	\$438,750	\$254,145		

Convert to Acetone Exclusively In Precleaning Step

Some of the solvents purchased by the hypothetical companies with the small and large operations are more expensive than acetone. In particular, NMP is a very expensive solvent. Converting exclusively to acetone could reduce solvent purchase costs. More important, using only one solvent makes it unnecessary to take measures to keep solvent streams separated. This can significantly reduce the cost of disposal. In addition, as discussed later, using only one solvent will allow more effective reutilization and use of the on-site distillation system since only one solvent needs to be dealt with in these cases.

In the case study examples, acetone, which is used for all the hoses in the third step, is classified as the default solvent. In effect, if hoses were cleaned in a manner that did not link them to a particular product, acetone is used as the default solvent in the cleaning operation. This assumption obviously depends on the products and their solubility in acetone. For some companies, their products may have better solubility in another solvent and a different solvent may be used as the default solvent. The approach to the analysis using acetone here provides the framework for the analysis such a company would have to conduct to evaluate the cost impact for their particular operation. A strong reason to consider acetone as the exclusive default solvent is that it is exempt from VOC regulations and is lower in toxicity than virtually all other organic solvents.

Pharmaceutical, biotechnology and chemical companies use a significant amount of solvent and they are likely to purchase them in drum or bulk quantities. To be conservative, the analysis assumed the solvents would be purchased in 55 gallon drums. The current cost of acetone is about \$500 per drum. The cost of NMP is more than double this cost, at \$1,100 per drum. Methylene chloride is about \$750 per drum currently and methanol, a less costly solvent, is priced at about \$225 per drum (PSC, 2011).

Table 2-1 summarized the amount of solvent purchases for the small and large case study operations. Based on these figures, the cost of purchasing solvent for the small operation amounts to \$1,351,704 annually. The cost of purchasing solvent for the large operation is double this amount or \$2,703,408 per year. Assuming acetone could replace the other solvents on a one for one volume basis, the annual cost of purchasing acetone as the only solvent for the small and large operations is \$1,181,818 and \$2,363,636 respectively.

The cost for solvent disposal is the other cost that must be considered in the use of solvents in the hose cleaning operation. The disposal costs that are relevant for this option are summarized in Table 2-2. The annual disposal cost for the solvents, assuming different solvents are used, is \$219,375 for the small operation and \$438,750 for the large operation. The annual disposal cost for the solvents assuming acetone is used exclusively would be 11 cents per pound for the total 117,000 gallons for the small operation and 234,000 gallons for the large operation, assuming a density for acetone of 6.6 pounds per gallon. In this case, since only one solvent is used, the bulk tank could be used for the solvent. This cost is \$84,942 for the small operation and \$169,884 for the large operation.

Table 2-3 summarizes the cost of continuing to use the four solvents for the flushing operation and the cost of converting to acetone exclusively. The figures show there are savings in both purchase costs and disposal costs. The values show that the cost of using acetone in the small and large operations results in a reduction over the cost of using the mixed set of solvents of about 19%. The reduction in cost that can be achieved for the small and large operations amounts to about \$300,000 annually and about \$600,000 respectively. This cost reduction is very significant.

Table 2-3 Comparison of Annual Cost of Hose Cleaning Operations				
Using Mixed Solve	nts and Using Acetone	e Exclusively		
	Use Mixed Solvent	Use Acetone Exclusively		
Small Operation				
Solvent Purchase Cost	\$1,351,704	\$1,181,818		
Solvent Disposal Cost	\$219,375	\$84,942		
Total Cost	\$1,571,079	\$1,266,760		
Large Operation				
Solvent Purchase Cost	\$2,703,408	\$2,363,636		
Solvent Disposal Cost	\$438,750	\$169,884		
Total Cost	\$3,142,158	\$2,533,520		

Change Order of Operations and Eliminate One Solvent Flush

The current practice is to first flush the hoses with one of the solvents, then flush the hoses with water, then flush the hoses with acetone and do a final flush with nitrogen. The option analyzed above involves flushing with acetone exclusively for the two solvent flushing steps. This option would involve eliminating the solvent precleaning step altogether and reversing the order of the water and solvent flushing steps. The technician would flush first with the deionized water then flush with acetone and then use nitrogen for the final flush. Companies considering this option would have to perform comparative analysis of the hoses flushed according to the original plan and the new option to ensure that sufficient contamination could be removed with the new option. In addition, they would have to determine there was no residual carryover of one product to the next which could result in a product recall. As discussed earlier, some contaminants that may be in the hoses will be soluble in water and some will be soluble in solvent. Using only one solvent flush—in this case, after the water flush—could provide sufficient cleaning capability with no carryover for the change.

Adopting this option would reduce the use of acetone by half compared with the option of converting exclusively to acetone. The purchase and disposal costs of this option are summarized in Table 2-4. For

comparison, the purchase and disposal costs of using the mixed solvents and using acetone exclusively are also presented in the table. The values show that eliminating one flush cuts the costs in half compared with the option of using acetone exclusively. It reduces costs by about 60% compared with the mixed halogenated and non-halogenated solvent use option. The cost savings for the option that eliminates one of the solvent flushes is more than \$900,000 per year compared with the mixed option for the small operation. For the large operation, the reduction is almost \$1.9 million per year.

Table 2-4 Comparison of Annual Cost of Hose Cleaning Operations				
Using Mixed Solvents, U	Jsing Acetone Exclu	sively and Eliminatin	g One Flush	
	Use Mixed	Use Acetone	Eliminate One	
	Solvents	Exclusively	Flush	
Small Operation				
Solvent Purchase Cost	\$1,351,704	\$1,181,818	\$590,909	
Solvent Disposal Cost	\$219,375	\$84,942	\$42,471	
Total Cost	\$1,571,079	\$1,266,760	\$633,380	
Large Operation				
Solvent Purchase Cost	\$2,703,408	\$2,363,636	\$1,181,818	
Solvent Disposal Cost	\$438,750	\$169,884	\$84,942	
Total Cost	\$3,142,158	\$2,533,520	\$1,266,760	

Reduce Use of Acetone in Flushing Operations

One progressive company analyzed their reactor tank cleaning operations and successfully reduced the amount of solvent they used to flush the tank to about one-third the solvent used originally in some of their cleaning operations. This option would involve reducing the amount of acetone used in the hose flushing operation by 40%. Instead of using 25 gallons of solvent in the hose flushing operation, only 10 gallons would be used. This option would be implemented after the option of eliminating one of the acetone flushes and would therefore result in about a 60% reduction in the purchase and disposal costs for that option. Again, the residue of contaminants in the hoses would have to be analyzed to ensure that adequate cleanliness could be achieved through adopting this option.

Table 2-5 summarizes and compares this option to the other options of using mixed solvent, using acetone exclusively and eliminating one of the flushes. This option reduces the cost by about 84 percent compared with the mixed solvent option and by 80 percent compared with the option of using acetone exclusively.

Reutilize Acetone

One large solvent supplier and recycler in California called PSC Environmental Services has a large customer that would be willing to purchase the spent solvent from a pharmaceutical company or chemical company depending on the quality of the acetone. The recycler, who is also a hazardous waste hauler, would pick up the spent acetone, analyze it, pay the company for it and repackage it and sell it to one or more other customers. The purity of the acetone must be sufficient for it to be reutilized rather than sent for disposal. The acetone would have to be water white and contain no more than three percent water. It should also not contain oils, greases or resins.

Table 2-5 Comparison of Annual Cost of Hose Cleaning Operations Using Mixed Solvents, Using Acetone Exclusively Eliminating One Flush and Reducing Acetone Use

	Use Mixed	Use	Eliminate One	Reduce Use
	Solvents	Acetone	Flush	of Acetone
Small Operation				
Solvent Purchase Cost	\$1,351,704	\$1,181,818	\$590,909	\$236,364
Solvent Disposal Cost	\$219,375	\$84,942	\$42,471	\$16,988
Total Cost	\$1,571,079	\$1,266,760	\$633,380	\$253,352
Large Operation				
Solvent Purchase Cost	\$2,703,408	\$2,363.64	\$1,181,818	\$472,727
Solvent Disposal Cost	\$438,750	\$169,884	\$84,942	\$33,977
Total Cost	\$3,142,158	\$2,533,520	\$1,266,760	\$506,704

The solvent used to flush the hoses at pharmaceutical, biotechnology and chemical companies is likely to still be of fairly high quality compared with other acetone sources, like autobody shops who use it for spray gun cleaning after coatings have been applied. Because the high technology sources use it in a one pass through operation, the solvent is unlikely to be highly contaminated. In the flushing operation, if the spent water stream is kept separate from the spent solvent stream, there is a smaller chance that the water content would exceed the 3% limit. Adding an extra nitrogen flush between the solvent and water flushing steps could provide further assurance that the water content of the solvent stream would remain low. The nitrogen would displace some of the water that would otherwise be left in the hose to be displaced by the solvent.

This option would be much more viable if the company converted exclusively to acetone. Assuming the quality of the used solvent is high enough, the recycler would purchase the solvent directly from the company and the company would not have to manifest it. Depending on the quality, the recycler could pay the company between 10 and 15 cents per pound. Assuming the midpoint of 12.5 cents per pound, under the acetone exclusive use scenario, the company would eliminate their waste disposal cost completely. In addition, the company would be paid 12.5 cents per pound for the waste which is now, actually, a product.

Table 2-6 compares the cost of disposal for all of the cases listed in Table 2-5 and this option. For the acetone reutilization case, the baseline acetone waste generation for the acetone exclusive use option was used for the calculation. This amounts to 117,000 gallons of spent acetone for the small operation and 234,000 gallons of spent acetone for the large operation. Based on a density of 6.6 pounds per gallon for acetone, the recycler would pay the facility \$96,525 for the spent solvent for the small operation and \$193,050 for the large operation. For the small operation, the company would eliminate the waste disposal cost of \$84,942 and receive a payment of \$96,525 for a net savings of \$181,467 annually. For the large operation, the company would eliminate the waste disposal cost of \$168,884 and receive a payment of \$193,050 for a net savings of more than \$361,934. In both cases, the savings is significant.

Table 2-6 Annual Disposal Cost for All Options and Credit for Reutilization				
Small Operation Large Operation				
Mixed Solvent Use	\$219,375	\$438,750		
Use Acetone Exclusively	\$84,942	\$168,884		
Eliminate One Flush	\$42,471	\$84,942		
Reduce Acetone Use	\$16,998	\$33,977		
Reutilize Acetone	(\$96,525)	(\$193,050)		

Recycle Acetone Off-Site

If the acetone is of reasonably high quality, which would be determined by analysis of the spent solvent by the recycling firm, the recycling company could recycle the solvent for reuse. Again, based on analysis that indicates a low level of contamination, the recycler would pay the company 10 cents per pound for the spent acetone. Since, in this case, the acetone would be recycled, the pharmaceutical, biotechnology or chemical company would be required to manifest the waste.

Table 2-7 shows the disposal cost comparison of the options from Table 2-6 and the off-site recycling option. Again, the baseline for the recycling option is the amount of waste generated from the exclusive use of acetone in the cleaning operation. In this case, the net savings for the small operation through adopting off-site recycling would amount to \$162,162 per year. The net savings for the large operation would be \$323,324 per year.

Table 2-7 Annual Disposal Cost for All Options and Credit for Reutilization and Recycling				
Small Operation Large Operation				
Mixed Solvent Use	\$219,375	\$438,750		
Use Acetone Exclusively	\$84,942	\$168,884		
Eliminate One Flush	\$42,471	\$84,942		
Reduce Acetone Use	\$16,998	\$33,977		
Reutilize Acetone	(\$96,525)	(\$193,050)		
Recycle Acetone Off-Site	(\$77,220)	(\$154,440)		

Purchase and Use On-site Still

This option involves purchasing and using an on-site distillation system for separating the acetone from the contaminants and reusing it in the same process. Many other types of companies ranging from dry cleaners and autobody shops and companies that have vapor degreasing operations to semiconductor manufacturers use distillation for recovery and reuse of solvents. DTSC regulations allow the use of an on-site distillation system without requiring a treatment permit if the solvent is reused in the same process.

IRTA analyzed the costs of purchasing and using a still to recover and reuse the solvent used in the hose cleaning operation. In this case, the starting point for the analysis was that the facility would first convert exclusively to acetone. The facility could still use other solvents in the hose cleaning operation but they would have to keep them segregated and only recycle the acetone, the most extensively used

solvent. The other solvents could also be distilled but separate systems would be required for each solvent.

Distillation processes are commonly used to separate solvent from contaminants so the solvent can be reused instead of shipped off-site for disposal. It involves using a tank with a heater containing the solvent that requires recycling and heating the solvent to its boiling point. In this case the boiling point of acetone is about 56 degrees C (133 degrees F). The solvent boils, forms a vapor and is condensed into a liquid. The contaminants might be small quantities of resins, oil, grease or carbon which have much higher boiling points than acetone. These heavier materials are left in the tank and they comprise the still bottom. The acetone and the contaminants have been separated and the acetone can be reused in the process. The still bottom is disposed of as hazardous waste.

IRTA obtained the cost information on the stills for the small and large hose cleaning operations from Progressive Recovery, Inc. (PRI, 2011). The company, located in Illinois, has been designing and manufacturing fluid process systems since 1983 and manufactures a wide range of distillation systems for general, ultra high purity and other specific applications. In practice, the chemical, biotechnology or pharmaceutical company would have to send a sample of the spent solvent to the still manufacturer for analysis before a system that would best handle the solvent could be selected. In this case, since the facilities are hypothetical, such sampling could not be done. As a result, to be conservative, IRTA and PRI selected a system that might be more expensive than needed.

The system is a single stage batch still which can accept a solvent input stream on a continuous basis. The small hose cleaning operation generates about 450 gallons per day of spent solvent and the large operation generates twice that much, 900 gallons per day. The still components that contact liquid are made of 303 stainless steel. It uses an Allen-Bradley PLC and carries a UL label. The power and control panel must be kept separate and the heater is explosion proof to deal with flammable solvents like acetone. It auto fills the tank so a continuous stream of solvent can be accepted. The system includes a small 60 gallon receiver tank which accepts the clean solvent; this tank can be piped to another larger or remote tank or drums for storage of the solvent until it is reused in the cleaning process. It has an automated shutdown so more solvent is not accepted when the solids receiver tank is full. The solids or still bottom would have to be periodically removed and put in drums for hazardous waste disposal. The frequency of removal would obviously depend on the level of contamination of the spent solvents. A picture of a typical distillation system is shown in Figure 2-2.

For the small hose cleaning operation, the still would need to process about 450 gallons per day. For the large hose cleaning operation, the still would have to process double this amount or 900 gallons per day. Assuming that the still could be operated for two shifts each day, a still with a capacity of 28 gallons per hour could be used for the small operation and a still with a capacity of 56 gallons per hour could be used for the large operation. The capital cost of the two stills, assuming the distillation system supplier would devote five days to calibrate the unit and train the operator and facility staff, is estimated at \$113,000 for the small still and \$154,000 for the larger still. The company purchasing the still would be responsible for the installation. The installation cost for each still could amount to \$5,000. The total capital and installed cost of the small and large systems would be \$118,000 and \$159,000 respectively.



Figure 2-2. Typical Distillation System

Many stills have a useful life of 20 years. To be conservative, the useful life of the stills is estimated at 15 years. Assuming a cost of capital of 4% and the 15 year life, the annualized cost of the small still is \$8,181 and the annualized cost of the larger still is \$11,024.

Routine maintenance of the stills includes changing the heat transfer oil which should be done every two years. The cost of changing the oil might amount to \$2,000 so the annual maintenance cost would be \$1,000.

Energy costs would include the energy to operate the system. The still could be powered by gas or electricity and gas is generally a less expensive option. Since pharmaceutical and chemical companies have access to gas, the still will be assumed to use gas. The small distillation system has a requirement of 123,000 BTU per hour and the large system has a requirement of 164,000 BTU per hour. Assuming each of the stills are operated for two shifts or 16 hours per day, five days per week, 52 weeks per year, the energy requirements for the small and large stills respectively would be 5,117 therms per year and 6,822 therms per year. The cost for gas presently is about 50 cents per therm. On this basis, the annual energy cost for operating the large and small stills is \$2,559 and \$3,441 respectively.

Even though the still operation would be largely automated, one of the company employees would be responsible for overseeing the process. This would involve making sure the system is operating properly, removing the still bottom when the unit is full and seeing to the maintenance. To be conservative, it was assumed that one or more employee would have to devote 10 hours per week to these activities. Assuming a 52 week per year operation, this would amount to 520 hours per year. Assuming a loaded labor rate of \$40 per hour, the annual labor cost is \$20,800.

The distillation system would be piped to its holding tank which would be filled when the cleaning operation was underway. The system would be open to the atmosphere when the still bottom is removed and this is a fairly frequent requirement. Emissions of solvent to the atmosphere are likely to be low; for analysis purposes, process and handling emissions were assumed to be 10% of the amount generated as waste. The other loss is solvent that remains in the still bottom; to be conservative, this solvent was neglected.

Based on these values and assuming the waste generation for the small hose cleaning operation is 117,000 gallons per year, the emissions would amount to 11,700 gallons per year. The solvent available for reuse would be 105,300 gallons per year. For the large hose cleaning operations, the figures would be twice those of the small hose cleaning operation. Emissions would be 23,400 gallons per year and the amount of solvent available for reuse would be 210,600 gallons per year.

The waste from the operation would consist of some solvent that cannot be completely removed and a significant amount of solids or sludge. A waste hauling company estimates the cost of disposal of the still bottom assuming a 5% acetone concentration at \$1 per pound. Assuming the contamination level in solvent used for the flushing operation of about 3%, the sludge in the small operation would amount to 3,510 gallons. Assuming a density for the sludge of nine pounds per gallon, 31,590 pounds of waste still bottom would require disposal at a cost of \$31,950. Using the same procedure for the large operation, the cost of the waste still bottom disposal would be \$63,180.

The solvent that is recycled using the still can be reused in the cleaning operation. Testing would be required to ensure that good quality control was maintained. The estimates given above indicate that there will be 105,300 gallons available for the small operation and 210,600 gallons available for the large operation. This recycled solvent can replace solvent that would otherwise have to be purchased. The company with the small operation purchases 130,000 gallons per year and the company with the large operation purchases 260,000 gallons per year. Again assuming a price for acetone of \$500 per drum and 55 gallons per drum, the acetone purchase costs for the small and large operations respectively are \$1,181,818 and \$2,363,636 annually. Based on replacing the virgin with the recycled acetone, the solvent purchase costs would be reduced to \$224,545 for the small operation and \$449,091 for the large operation annually.

Table 2-8 summarizes the costs for implementing the option of using an on-site still for the large and small operations. In both cases, the costs of this option are compared with the baseline case which involves using acetone exclusively in the cleaning operation. The costs represent the additional costs incurred through purchase of the distillation system and these are not applicable to the baseline case. In these instances, the table includes a dash.

The figures of Table 2-8 show that the major savings from adopting this option is in avoided purchase costs for the acetone. The recycled solvent can be used in place of virgin solvent. The savings through

Table 2-8 Annualized Cost Comparison for Use of On-Site Distillation System					
	Small Operation Large Operation				
	Baseline	Still Option	Baseline	Still Option	
Capital/Installation Cost	-	\$8,181	-	\$11,024	
Maintenance Cost	-	\$1,000	-	\$1,000	
Energy Cost	-	\$2,559	-	\$3,441	
Labor Cost	-	\$20,800	-	\$20,800	
Disposal Cost—Solvent	\$84,942	-	\$169,884	-	
Disposal Cost—Still Bottom	-	\$31,950	-	\$63,180	
Solvent Purchase Costs	\$1,181,818	\$224,545	\$2,363,636	\$449,091	
Total Costs	\$1,266,760	\$289,035	\$2,533,520	\$548,536	
Note: Baseline assumes aceton					

purchasing the distillation system amounts to more than 77% compared with the baseline case of using acetone exclusively for the small operation and about 78% for the large operation. The savings, in the case of the small operation, amount to almost \$1 million annually and the savings for the large operation are nearly \$2 million annually.

Comparison of Options for Reducing Solvent Use

Table 2-9 summarizes the costs and net savings for the options analyzed here. The highest savings can be realized by purchasing and using an on-site still. This follows from the fact that a significant amount of solvent is used in the cleaning operations on a continuous basis. The other option that is promising is to reutilize the acetone. Although the savings from this option are lower, it offers a significant savings without the need for purchasing equipment or having facility staff operate it. The savings are almost as high for the off-site recycling option which is also a good one.

Table 2-9 Annual Savings Compared with Baseline Option of Using Acetone Exclusively				
Small Operation Large Operation				
Eliminate One Flush	\$42,471	\$84,942		
Reduce Acetone Use	\$67,944	\$134,907		
Reutilize Acetone	\$181,467	\$361,934		
Recycle Acetone Off-Site	\$162,162	\$323,324		
Recycle Acetone On-Site	\$977,725	\$1,984,984		

There are several issues involved for a facility in selecting the best option for their circumstances. The company would have to conduct comparative analysis of the residue to decide whether it is possible to eliminate one of the solvent flushes or to significantly reduce the acetone use in the cleaning operation. If the residue were too high, it might not be possible to eliminate one of the flushes. If the acetone used in the cleaning could not be reduced by 60%, it might be reduced by 30%; any reduction in acetone use would be of benefit.

If the solvent is heavily contaminated with oils, resins or other materials from the cleaning operation, reutilizing or recycling the acetone off-site would not be viable. In both cases, the quality of the acetone would need to be relatively high and contamination low; the recycling firm would simply not accept the acetone in cases of heavy contamination except for disposal through incineration. On the other hand, the on-site recycling option would still be acceptable even if the solvent is fairly heavily contaminated. Resins can cause problems in distillation systems and it is likely, in cases of high resin concentrations, a more expensive still would be required. Higher contamination levels would also yield less solvent from the on-site recycling operation so the credit for replacement of virgin solvent would be less and the cost of disposal for the still bottom would be higher.

OPTIONS FOR ELIMINATING SOLVENT USE

In another study, screening tests of several potential alternatives were performed on soiled coupons (Wolf, 2011). The results of the tests verified that two water-based alkaline cleaners performed well in cleaning a pharmaceutical intermediate, oil and grease and carbon. Similar soils could be encountered in a hose cleaning operation at a chemical, pharmaceutical or biotechnology company. The two cleaners, CIP 100/ProKlenz and Metalnox M6321, are cleaners that have been used by high technology companies for maintenance cleaning purposes. In the earlier study, the CIP 100/ProKlenz performed well on both the pharmaceutical intermediate and the carbon soil. The Metalnox M6321 performed well on the oil and grease and the carbon soil (Wolf, 2011).

Scaled-up testing of these cleaners has not been performed for process hose cleaning operations. Because the two cleaners performed well in screening tests, however, IRTA analyzed the cost of using them in place of the solvents that are traditionally used. The suppliers of the cleaners were helpful in providing information on optimizing the use of the cleaners and their cost.

Conversion to CIP 100/ProKlenz

An MSDS for CIP 100 is provided in the Appendix. It indicates the product is an alkaline cleaner that also contains surfactants. An MSDS for ProKlenz is also provided in the Appendix. This booster product also contains surfactants in addition to hydrogen peroxide. In the screening tests, the CIP 100/ProKlenz cleaner was used at a concentration of 2% resulting in an as applied pH of 12.54. In the analysis, it was assumed that the cleaner would contain 1% each of the CIP 100 and the ProKlenz additive. Steris, the supplier of the CIP 100 and the ProKlenz booster products, indicates that an equal concentration of each one of the components is a viable formulation (Steris, 2011).

Since scaled up testing was not conducted, it is difficult to know how much of the water-based cleaner would need to be used in the hose flushing operation. For purposes of analysis, IRTA assumed two cases. In the first case, 25 gallons of the cleaner would be required for one flush. The water-based cleaner would then have to be rinsed from the hose with 25 gallons of water, the same amount of water used for the flushing with the solvents. Nitrogen would then be used to dry the hoses. In the second case, it was assumed that 10 gallons of the cleaner would be sufficient for flushing the hoses. This would be followed by the water rinse and the nitrogen drying steps. Table 2-10 presents the information on the amount of cleaner required for the flushing operation in the two cases.

The values of Table 2-10 indicate that the 650 gallons each of the CIP 100 and the ProKlenz booster are needed for the small hose cleaning operation and 1,300 gallons each are needed for the large hose cleaning operation annually for the first case where 25 gallons are used to flush each hose. Steris provides 55 gallon drums of the two cleaners and, since the volumes of each cleaner that are required

Table 2-10 Use of CIP 100/ProKlenz Detergent in Hose Flushing Operation					
Small Operation Large Operation					
Number of Hoses	2,600	5,200			
Case One					
Cleaner Use	25 gallons/hose	25 gallons/hose			
Cleaner Volume	65,000 gal/year	130,000 gal/year			
Cleaning Agent Use	1,300 gal/year	2,600 gal/year			
Case Two					
Cleaner Use	10 gallons/hose	10 gallons/hose			
Cleaner Volume	26,000 gal/year	52,000 gal/year			
Cleaning Agent Use	520 gal/year	1,040 gal/year			

are high, the pharmaceutical or chemical company would likely purchase the cleaners in drum quantities. The price of a 55 gallon drum of CIP 100 is \$1,422 and the price of a 55 gallon drum of ProKlenz booster is \$1,644 (Steris, 2011). Based on these prices, the cost of using the CIP 100 and the ProKlenz booster respectively in the small operation is \$16,805 and \$19,429 annually. The total cost of the cleaning agents is \$36,234. The cost of using the two cleaners in the large operation is \$33,611 for the CIP 100 and \$38,858 for the ProKlenz booster. The total cost, in this case, is \$72,469.

The values of Table 2-10 for the case where the flushing volume is reduced to 10 gallons per hose are 520 gallons per year and 1,040 gallons per year for the small and large operations respectively. Using the cleaner prices given above, the cost of purchasing the CIP 100 and the ProKlenz booster in the small operation would amount to \$6,722 and \$7,772 annually for a total annual cost of \$14,494. For the large operation, the cost of purchasing the CIP 100 and the ProKlenz booster are \$13,444 and \$15,543 respectively for a total annual cost of \$28,987.

The water cleaning formulations would be blended with deionized water for the flushing operation. A deionizing water system consisting of cation and anion exchange beds and a carbon pretreatment which would supply water of one megohm quality could be installed. The capital cost of a system which would provide 250 gallons per day for the small operation and 500 gallons per day for the large operation are estimated at \$3,500 and \$6,500 respectively. Assuming a cost of capital of 4% and a 10 year life for the system, the annualized cost for the small and large systems respectively would be \$364 and \$676. The operating cost for the systems would be purchase of hydrochloric acid and sodium hydroxide for bed regeneration once a week. The operating cost for the small and large systems would be \$250 and \$500 per month respectively or \$3,000 and \$6,000 per year. The yearly cost, including the annualized cost for purchasing the system and the operating cost for the small system, would be \$3,364. For the large system, it would be \$6,676.

The cleaners would have to be preblended in tanks prior to their use in the flushing operation. For the case where the flushing requires 25 gallons per hose, the small operation involves flushing 10 hoses per day so a tank of the cleaner holding at least 250 gallons would be needed for the flushing operation; a tank holding 500 gallons of the cleaner would have to be prepared for the large operation. The tanks would be made of plastic and they would have covers. The small tank would be 40 feet by 40 feet by 40 feet in dimensions and it would have two 24 kW stainless steel heaters. The large tank would be 80 feet by 40 feet by 40 feet in dimensions and would have four 24 kW stainless steel heaters. Both tanks would have digital temperature control, a low level indicator and an over temperature safety reset

option. The heat up time would be 1.5 hours and the heaters and controls are based on 480 volt three phase power.

The cost of the small 250 gallon tank including the heaters is estimated at \$6,850. Assuming a cost of capital of 4% and a 10 year life for the tanks and heaters, the annualized cost would amount to \$712. The cost of the large 500 gallon tank is estimated at \$13,700. Again, assuming a 4% cost of capital and a 10 year life, the annualized cost would be \$1,425.

A worker would have to blend the cleaners and this might require one hour per day for the small operation and two hours per day for the large operation. Assuming a labor rate of \$40 per hour, five days per week and 52 weeks per year, the labor cost for the blending would amount to \$10,400 per year for the small operation and \$20,800 for the large operation. For the case where only 10 gallons per hose are needed, the labor cost would be 40% of the labor cost where 25 gallons are required. In this case, the labor cost of the small operation would be \$4,160 and the labor cost for the large operation would be \$8,320.

All cleaners perform better at elevated temperature. Water-based cleaners, in particular, are significantly better cleaners at higher temperatures. The results of the screening tests at the room and elevated temperature verified this point. The cleaner should be preheated before it is used in the flushing operation. This means the cleaner would need to be held at an elevated temperature for the eight hour shift when the cleaning is performed. As discussed above, the small tank for holding the heated water has two 24 kW heaters and the large tank has four 24 kW heaters. Both tanks would require 1.5 hours for preheating the cleaner to the higher temperature. After the temperature was achieved, the heaters would cycle on for 10 to 15 minutes per hour over the eight hour day. Assuming a 15 minute on cycle, the total time over the day, including the 1.5 hour preheating, would be 3.5 hours. Based on a five day week, 52 weeks per year, the total time over a year for the heater operations would be 910 hours. The small tank energy requirement would be 43,680 kWh per year and the large tank energy requirement would be 87,360 kWh per year. Assuming an energy cost of 10 cents per kWh, the energy cost for the small system would be \$4,368 annually and the cost for the large system would be \$8,736 per year.

Flushing with the water-based cleaner generates waste spent cleaner which may contain contaminants from the hoses. Very little of the water formulations used in the process would evaporate. For purposes of analysis, it was assumed that the same volume of cleaner used in the flushing operation would be waste. Two options for disposal of the wastewater were considered. The first option is that the water waste is shipped off-site for disposal. The second option is that the water waste is treated in a wastewater treatment system.

Because the operation is a one pass through, the water would only be used once for the hose flushing operation. As was assumed for the solvents, the water is not likely to be heavily contaminated. The cost of off-site disposal of the water, assuming it is not classified as hazardous waste, is \$1 per gallon (PSC, 2011). On this basis, the cost of disposing of the water from the small operation would be \$65,000 annually and the cost of disposing of the water from the large operation would be \$130,000 annually. If the wastewater that is generated is heavily contaminated with components including solvents, it would require incineration at a much higher cost of about \$1 per pound (PSC, 2011). It is unlikely that solvents would be in the spent water cleaners since they would no longer be used in the cleaning operation. Even so, this case was evaluated to be thorough. Assuming a midrange higher cost of 50 cents per

pound, the cost of disposal of the wastewater for the small and large operations respectively would be \$270,725 and \$541,450 if the wastewater were heavily contaminated.

Table 2-11 summarizes the annual costs for the high flushing volume and low flushing volume cases for the small and large operations. For the cost of flushing with the lower volume, each cost element is assumed to be 40% of the cost of flushing with the higher volume for both the small and large operations.

Table 2-11						
	Annual Cost Comparison for CIP					
	100/ProKlenz Cleanin	g Agent Assuming Of	f-Site Disposal			
	High Volume Flushing		Low Volume Flushing			
	Small Operation	Large Operation	Small Operation	Large Operation		
Cleaner Cost	\$36,234	\$72,469	\$14,494	\$28,987		
Deionized Water Cost	\$3,364	\$6,676	\$1,346	\$2,670		
Tank Cost	\$712	\$1,475	\$285	\$590		
Labor Cost	\$10,400	\$20,800	\$4,160	\$8,320		
Energy Cost	\$4,368	\$8,736	\$1,747	\$3,494		
Cleaner Off-Site Disposal	\$65,000-\$270,725	\$130,000-\$541,450	\$26,000-\$108,290	\$52,000-216,580		
Total Cost	\$120,078-\$325,803	\$240,156-\$651,606	\$48,032-\$130,322	\$96,061-\$260,461		

Instead of shipping the spent wastewater off-site for disposal, the company would be more likely to treat it in an existing wastewater treatment system. Virtually all pharmaceutical, biotechnology and chemical manufacturers would already have such a system. Assuming the surfactants in the water-based cleaner that was selected would be able to be degraded easily in the system, the incremental cost for treatment of 250 or 500 gallons per day would be negligible. Under this assumption, Table 2-12 shows the cost comparison for the small and medium high and low volume flushing operations using the CIP 100/ProKlenz cleaning agent. The cost of using the on-site wastewater treatment system is significantly lower than the cost of shipping the water waste off-site.

Table 2-12 Annual Cost Comparison for CIP 100/ProKlenz Cleaning Agent Assuming On-Site Treatment					
	High Volume Flushing		Low Volume Flushing		
	Small Operation	Large Operation	Small Operation Large Opera		
Cleaner Cost	\$36,234	\$72,469	\$14,494	\$28,987	
Deionized Water Cost	\$3,364	\$6,676	\$1,346	\$2,670	
Tank Cost	\$712	\$1,475	\$285	\$590	
Labor Cost	\$10,400	\$20,800	\$4,160	\$8,320	
Energy Cost	\$4,368	\$8,736	\$1,747	\$3,494	
Total Cost	\$55,078	\$110,156	\$22,032	\$44,061	

Conversion to Metalnox M6321

The cost analysis for the Metalnox M6321 cleaning agent is similar to the cost analysis for the CIP 100/ProKlenz cleaner. The price of the Metalnox M6321, however, is different. In the earlier study which involved screening tests, the M6321 performed best at elevated temperature and at 10%

concentration (Wolf, 2011). According to Kyzen, the supplier of the M6321, the cost of a drum of the material is \$585 (Kyzen, 2011). For the case where 25 gallons of cleaner are used to flush the hoses, 65,000 gallons and 130,000 gallons are used annually for the small and large operations respectively. Assuming a 10% concentration, the annual cost of purchasing the cleaner would be \$69,136 for the small operation and \$138,273 for the large operation. For the case where 10 gallons are used for flushing, the annual cost of purchasing the cleaner for the small and large operations is \$27,655 and \$55,309 respectively. The labor cost, the energy cost, the disposal cost and the wastewater treatment cost for this cleaner would be the same as the comparable costs for the CIP 100/ProKlenz cleaner.

Table 2-13 summarizes the costs for Metalnox M6321 for the case where the wastewater is shipped off-site for disposal. The cost of using this cleaner is higher than the cost of using the CIP 100/ProKlenz because the cost of the cleaner itself is higher. In the earlier study on screening tests, the 5% concentration of the Metalnox M6321 performed almost as well as the CIP 100/ProKlenz formulation (Wolf, 2011). If the cost of purchasing the 5% concentration rather than the 10% concentration were used in Table 2-11, the cost of using the Metalnox cleaner would be slightly lower than the cost of using the CIP 100/ProKlenz cleaner.

Table 2-13 Annual Cost Comparison for Metalnox M6321 Cleaning Agent Assuming Off-Site Disposal					
	High Volume Flushing		Low Volume Flushing		
	Small Operation	Large Operation	Small Operation Large Operation		
Cleaner Cost	\$69,136	\$138,273	\$27,655	\$55,309	
Deionized Water Cost	\$3,364	\$6,676	\$1,346	\$2,670	
Tank Cost	\$712	\$1,475	\$285	\$590	
Labor Cost	\$10,400	\$20,800	\$4,160	\$8,320	
Energy Cost	\$4,368	\$8,736	\$1,747	\$3,494	
Cleaner Off-Site Disposal	\$65,000-\$270,725	\$130,000-\$541,450	\$26,000-\$108,290	\$52,000-\$216,580	
Total Cost	\$152,980-\$358,705	\$305,960-\$717,410	\$61,193-\$142,151	\$122,383-\$286,963	

Table 2-14 summarizes the costs for Metalnox M6321 for the case where the wastewater is treated onsite. Again the cost of using this cleaning agent is slightly lower than the cost of using the CIP 100/ProKlenz cleaner.

Table 2-14 Annual Cost Comparison for Metalnox M 6321 Cleaning Agent Assuming On-Site Treatment					
	High Volume Flushing		Low Volume Flushing		
	Small Operation	Large Operation	Small Operation Large Operation		
Cleaner Cost	\$69.14	\$138,273	\$27,655	\$55,309	
Deionized Water Cost	\$3,364	\$6,676	\$1,346	\$2,670	
Tank Cost	\$712	\$1,475	\$285	\$590	
Labor Cost	\$10,400	\$20,800	\$4,160	\$8,320	
Energy Cost	\$4,368	\$8,736	\$1,747	\$3,494	
Total Cost	\$87,980	\$175,960	\$35,193	\$70,383	

Comparison of Conversion Options to Baseline Case

The baseline case is exclusive use of acetone. Table 2-15 shows the cost comparison of the baseline case and the conversion to CIP 100/ProKlenz for the small and large operations. The values for the conversion option are those for the high volume flushing operation with on-site wastewater treatment. The values show that the cost of using a water-based cleaner is almost 23 times lower than the cost of using acetone exclusively for the flushing operation. If the higher cost option of conversion to the water-based cleaner with high cost off-site wastewater disposal were considered, the cost of using the solvent for flushing is still almost 3.9 times higher than the cost of using the water-based cleaner.

Table 2-15 Annualized Cost Comparison of Solvent Baseline and Water-Based Cleaning Option With High Volume Flushing				
	Small	Operation	Large Operation	
	Baseline	Conversion To	Baseline	Conversion To
		CIP 100/ProKlenz	1	CIP 100/ProKlenz
Cleaner Cost	-	\$36,234	-	\$72,469
Deionized Water Cost	-	\$3,364	-	\$6,676
Tank Cost	-	\$712	-	\$1,475
Labor Cost	-	\$10,400	-	\$20,800
Disposal Cost—Solvent	\$84,942	-	\$169,884	-
Energy Cost	-	\$4,368	-	\$8,736
Solvent Purchase Costs	\$1,181,818	-	\$2,363,636	-
Total Costs	\$1,266,760	\$55,078	\$2,533,520	\$110,156

UNCERTAINTIES IN THE COST ANALYSIS

It is challenging to account for all the costs and benefits in an analysis like the one performed here. Scaled-up testing of the alternatives was not conducted, for example, and this means that there are many unknowns in the assumptions. In analyzing the cost of adopting the options, there may be some cases where costs that would be incurred were ignored. In other cases, there might be cost savings through adopting an option that were not taken into account.

As an example of the first case, depending on the characteristics of the facility, additional tanks, piping and instrumentation may be required to implement some of the options and these costs were not evaluated. As another example, if a facility has an on-site wastewater treatment facility and converts to a water-based cleaner, the spent cleaner could be treated in the system. The increase in wastewater generation was small and it was ignored in the analysis. Depending on the volume of wastewater treated by the facility, this may not be valid. As another example of the first case, CIP 100/ProKlenz may not be an appropriate cleaner for all the hose cleaning operations in a facility as was assumed in the cost analysis. Another example is that reversing the operations to flush with water first and solvent second may require an additional nitrogen flush between steps and the cost of the nitrogen was not included in the analysis. Yet another example is that no costs for validation were included and, depending on the company, they could be significant. On the other hand, as an example of the second case, cutting down the number of steps and eliminating the precleaning step would lead to a savings in labor and this was not taken into account.

One uncertainty that concerns the hazardous waste regulations could arise for some companies that wish to adopt the option of on-site recycling. As indicated earlier, many companies use distillation to separate solvent from contaminants and the solvent is reused in the same process replacing virgin solvent. Examples of the types of operations where solvent is recycled are autobody shops with spray gun cleaning systems, dry cleaners using various solvents for garment cleaning and companies with vapor degreasing operations. Treatment of hazardous waste is not allowed in California unless the company obtains a tiered permit or is otherwise authorized by DTSC for such an operation. Recycling the solvent is not considered treatment if the solvent is reused in the same process but DTSC may have additional requirements for pharmaceutical, biotechnology and chemical companies to recycle solvent for reuse in the hose cleaning operation. One example is that DTSC might require hard piping to ensure the solvent is reused for hose cleaning. This should not be a problem for the case analyzed here, however, since the hose flushing operation involves metering the solvent from a source like a tank where the recycled solvent could be held.

In the analysis, IRTA identified all the cost components that were determined in the analysis of each option. This transparency allows calculations using different assumptions for companies interested in evaluating the options for their specific situation. It's worth noting that, even if the costs for the options are double the cost assumed here, they would still be cost effective compared with the baseline case and are worth pursuing for operations where they seem practical.

III. RESULTS AND CONCLUSIONS

This project focused on finding safer alternatives to solvents used for cleaning reactor tanks and associated equipment like valves, process hoses and driers. The results should be useful as a starting point for more extensive scaled-up individual testing for companies like pharmaceutical, biotechnology and chemical manufacturers. The project involved conducting a detailed analysis of a number of options for reducing or eliminating the use of solvents for process hose cleaning operations.

Pharmaceutical and chemical companies use process hoses to transfer product to and from reactor tanks and other equipment. Companies with many batch operations often have a central hose cleaning station for flushing the hoses between runs of different product. During this project, IRTA analyzed several different options for reducing or eliminating the use of solvents used in the hose cleaning operation.

Two hypothetical operations were analyzed, one that involved cleaning 10 hoses per day and another that involved cleaning 20 hoses per day. The hypothetical plants were using four solvents for their hose cleaning including methylene chloride, NMP, methanol and acetone. Some of these solvents are VOCs and some are toxic in various ways. Methods of reducing the use of the solvents and adopting low VOC, low toxicity solvents were evaluated. Options for eliminating the use of solvents altogether and using water-based cleaners were also evaluated. The Table 3-1 summarizes and compares the annualized costs of the options that reduce solvent use and the conversion options.

Table 3-1					
Annualized Cost Comparison of Options for Reducing or Eliminating Solvent Use					
	Annualized Cost				
	Small	Large			
	Operation	Operation			
Mixed Halogenated/Non-Halogenated Solvent Use	\$1,571,079	\$3,142,158			
Exclusive Use of Acetone, High Volume Flushing	\$1,266,760	\$2,533,520			
Eliminate One Flush	\$633,380	\$1,266,760			
Lower Volume Flushing	\$253,352	\$506,704			
Reutilize Acetone	\$1,085,293	\$2,171,577			
Recycle Acetone Off-Site	\$1,104,598	\$2,210,196			
Recycle Acetone On-Site	\$289,035	\$548,536			
Convert to CIP 100/ProKlenz Water-Based Cleaner, High Volume Flushing	\$55,078	\$110,156			
Convert to CIP 100/ProKlenz Water-Based Cleaner, Low Volume Flushing	\$22,032	\$44,061			
Convert to Metalnox M6321 Water-Based Cleaner, High Volume Flushing	\$87,980	\$175,960			
Convert to Metalnox M6321 Water-Based Cleaner, Low Volume Flushing	\$35,193	\$70,383			

The options listed in Table 3-1 can be considered in terms of their timeframe for adoption. Three of the short-term options are using acetone exclusively, eliminating one flush and reducing the volume of the one remaining flush. Validation testing in the facility would allow these options to be implemented in a short timeframe. Virtually all pharmaceutical, biotechnology and chemical manufacturing companies have a laboratory for quality control testing since stringent quality standards must be continually met. Comparative testing would allow a determination of the cleanliness achieved with the use of these three

options compared to the mixed halogenated/non-halogenated solvent use. The testing could be performed in a short timeframe and the options that were viable could be implemented relatively quickly.

Two of the other options—reutilizing the acetone and recycling the acetone off-site—are also short-term options. The off-site recycler could determine very quickly if either option were viable by analyzing a sample of the spent solvent provided by the pharmaceutical, biotechnology or chemical company. This would require minimal effort on the part of the company and could be done in a matter of days.

One of the options, on-site recycling, is a medium-term option. The company would have to begin work with a still manufacturer to determine the size and type of still that would be best for the specific operation. The company would be required to send samples of the spent solvent to the still manufacturer. If an off-the-shelf still could be used, the option could be implemented fairly quickly.

The last four options, the conversions to the water-based cleaners, would be longer-term options. Companies would have to conduct preliminary and validation testing to assess the cleaning capability of the alternatives for their important products. The results of the screening tests in the earlier study (Wolf, 2011) should be useful for informing other screening test efforts. In some cases, companies might use the screening test results from the earlier work directly and move to scaled-up testing quickly. Companies would then have to determine which of their products and reactors could undergo the substitution first and begin implementing the change where it was viable.

The values of Table 3-1 can also be considered in terms of their comparative cost. They illustrate that the best overall option for companies is to convert to water-based cleaners. This option is the lowest cost if the company has an on-site wastewater treatment facility. Even if the company does not have a treatment system, if the spent water-based cleaner is not heavily contaminated and the off-site disposal cost is fairly low, the option is still a good one. The figures in Table 3-1 are for the low volume flushing operation using the water-based cleaner. Even if a higher volume of the cleaner is required, the option is still comparatively good.

Moving to lower volumes of solvent for flushing is also an attractive operation. Whether the company is using solvent or a water-based cleaner, it makes sense to use as low a volume of cleaner as possible without jeopardizing the cleaning quality.

On-site recycling of the solvent also is a very attractive option that can reduce costs significantly. In the meantime, while the company explored this option, the company could begin reutilizing or sending the solvent for off-site recycling if such options were found to be viable. The off-site options are good ones because they would require so little effort for a great deal of benefit if the spent solvent is of reasonably high quality.

The values in Table 3-1 may not exactly represent the costs of any particular pharmaceutical, biotechnology or chemical company's hose cleaning operation. They are a guide, however, for comparative evaluation of options. Several different assumptions were made in the analysis and these could easily be changed based on the exact characteristics of the operation in a given company.

IV REFERENCES

(Wolf, 2011) Safer Alternatives for the Chemical, Pharmaceutical and Biotechnology Industries: Process Hose Cleaning, Katy Wolf, Institute for Research and Technical Assistance, September 2011.

(PSC, 2011) Conversations with Craig Isaacs from PSC Environmental Services, Inglewood, California, 2011.

(PRI, 2011) Conversations with Rick Allen, Progressive Recovery, Inc., Dupo, Illinois, 2011.

(Steris, 2011) Conversations with Stacey Betts and Paul Lopolito from Steris Corporation, Mentor, Ohio, 2011.

(Kyzen, 2011) Conversation with staff from Kyzen, Nashville, Tennessee, 2011.