US Army Corps of Engineers
Construction Engineering
Research Laboratories

USACERL Technical Report EP-93/05
September 1993
Technology for Waste Solvent/Oil Recycling

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Aqueous Alkaline Cleaners: An Alternative to Organic Solvents

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Cleaning metal parts is a common task at U.S. Army installations. Because solvents are generally used for this service, large quantities of hazardous waste are generated daily at posts around the world. The environmental impacts and escalating cost of waste disposal have prompted the Department of Defense (DOD) to initiate programs seeking safe and efficient methods to reduce solvent waste generation. In response, the U.S. Army Construction Engineering Research Laboratories (USACERL) initiated a study to investigate the use of alkaline cleaners as an alternative to organic solvents now being used.

Alkaline cleaning is an age-old technology used extensively throughout the industry. Recently, the use of alkaline cleaners has increased due to the growing awareness of environmental and personnel safety concerns associated with chlorinated and petroleum-based solvents (i.e., 1,1,1-trichloroethane and Stoddard solvent). Properties associated with alkaline cleaners (i.e., nontoxic, nonvolatile, noncombustible, and biodegradable) make them an environmentally acceptable alternative for use in metal parts cleaning.

The USACERL analysis found that aqueous alkaline cleaning systems can be an alternative for degreasing operations at U.S. Army installations. Due to the unique operating conditions at every base, each system should be thoroughly tested. Preliminary testing will ensure a proper system design that will benefit both the installation and the environment.

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FOREWORD

This research was funded by the U.S. Army Center for Public Works (USACPW) under Project 4A162720A896, "Base Facility Environmental Quality"; Work Unit TQ1, "Technology for Waste Solvent/Oil Recycling." The technical monitor was Malcolm McLeod, CECPW-FU-S.

This manuscript was submitted by Robert Bird in partial fulfillment of the requirements for the degree of Master of Science in Environmental Engineering in Civil Engineering in the Graduate College of the University of Illinois at Urbana-Champaign. The advisor of the thesis was Dr. Roger A. Minear.

Technical guidance and support were provided by Bernard Donahue and the Environmental Engineering Division (EP) of the Environmental Sustainment Laboratory (EL), U.S. Army Construction Engineering Research Laboratories (USACERL). Dr. Edgar Smith is Acting Chief, CECER-EP, and Dr. Edward W. Novak is Acting Chief, CECER-EL. The USACERL technical editor was Linda L. Wheatley, Information Management Office.

LTC David J. Rehbein is Commander of USACERL and Dr. L.R. Shaffer is Director.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave Blank)	2. REPORT DATE September 1993	3. REPORT TYPE AND DATES COVERED Final

4. TITLE AND SUBTITLE
Aqueous Alkaline Cleaners: An Alternative to Organic Solvents

5. FUNDING NUMBERS
4A162720
A896
TQ1

6. AUTHOR(S)
Robert Wolfgang Bird and Bernard A. Donahue

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
U.S. Army Construction Engineering Research Laboratories (USACERL)
P.O. Box 9005
Champaign, IL 61826-9005

8. PERFORMING ORGANIZATION REPORT NUMBER
TR-EP-93/05

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U.S. Army Center for Public Works (USACPW)
ATTN: CECPW-FU-S
Bldg. 358
Fort Belvoir, VA 22060-5516

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

Copies are available from the National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161.

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

Cleaning metal parts is a common task at U.S. Army installations. Because solvents are generally used for this service, large quantities of hazardous waste are generated daily at posts around the world. The environmental impacts and escalating cost of waste disposal have prompted the Department of Defense (DOD) to initiate programs seeking safe and efficient methods to reduce solvent waste generation. In response, the U.S. Army Construction Engineering Research Laboratories (USACERL) initiated a study to investigate the use of alkaline cleaners as an alternative to organic solvents now being used.

Alkaline cleaning is an age-old technology used extensively throughout the industry. Recently, the use of alkaline cleaners has increased due to the growing awareness of environmental and personnel safety concerns associated with chlorinated and petroleum-based solvents (i.e., 1,1,1-trichloroethane and Stoddard solvent). Properties associated with alkaline cleaners (i.e., nontoxic, nonvolatile, noncombustible, and biodegradable) make them an environmentally acceptable alternative for use in metal parts cleaning. The USACERL analysis found that aqueous alkaline cleaning systems can be an alternative for degreasing operations at U.S. Army installations. Due to the unique operating conditions at every base, each system should be thoroughly tested. Preliminary testing will ensure a proper system design that will benefit both the installation and the environment.

14. SUBJECT TERMS
hazardous waste
waste disposal
metal cleaning
environmental impact analysis
aqueous alkaline cleaning systems
alkaline cleaners

15. NUMBER OF PAGES
88

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT SAR

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std 239-18
298-102

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Introduction

1.1 Overview

Cleaning metal parts is a common task at U.S. Army installations. Because solvents are generally used for this service, large quantities of hazardous waste are being generated daily at posts around the world. The environmental impacts and escalating cost of waste disposal have prompted the Department of Defense (DOD) to initiate programs seeking safe and efficient methods to reduce solvent waste generation.

The most common solvents used in metal parts cleaning are 1,1,1-trichloroethane (TCA) and Stoddard solvent (referred to as PD-680 at military installations). The wastes generated by these solvents are listed by the U.S. Environmental Protection Agency (USEPA) as hazardous and are subject to current land disposal restrictions. As a result, once the solvents are contaminated, procedures set forth by the Resource Conservation and Recovery Act (RCRA) (amended in 1984) must be followed to ensure proper disposal. This legislation has forced generators of hazardous waste to comply with the new standards of waste disposal and institute waste minimization programs.

The amendments have prompted the Army to investigate procedures that will lead to waste minimization, as opposed to end-of-pipe methods. The U.S. Army Construction Engineering Research Laboratories (USACERL) has been examining techniques for reducing solvent waste. These techniques include alternative solvent substitution when applicable, waste solvent minimization, waste solvent recycling, and waste solvent disposal. The Army's goal is to reduce hazardous waste generation by implementing minimization programs at all its installations. This philosophy is consistent with DOD policy to reduce costs associated with waste disposal and protection of the environment.

Under the strict regulations of the RCRA and the Comprehensive, Environmental Response, Compensation, and Liability Act (CERCLA), the Army's continued use of Stoddard solvent and TCA would not be economically beneficial. The long-term costs associated with ultimate disposal of hazardous waste keep rising as regulations on land disposal tighten. The replacement of Stoddard solvent and TCA with an environmentally safe cleaner would relieve the Army of much of the financial burden of waste disposal.

A previous study[25] was performed by USACERL to determine if semi-aqueous terpene cleaner could be used as a substitute for organic solvents. This report examines the possibility of employing an alkaline cleaner as an alternative to the organic solvents now being used. To achieve this, the cleaner should:

- be environmentally safe (i.e., not classified as a hazardous waste)
- have low disposal cost
- be biodegradable
- meet current Army cleaning standards.

Installation of the cleaner process also must be economically feasible.

1.2 Objective

The objective is to develop a methodology for estimating cost and environmental benefits of substituting alkaline cleaner for organic solvent used in metal parts cleaning. Stoddard solvent and TCA will be compared to a brand of alkaline cleaner specified for industrial cleaning operations. The methodology for selecting and evaluating the alternative solvent considers cleaning efficiency, environmental benefits and overall cost.

1.3 Approach

1. Review literature for information on Stoddard solvent and TCA (e.g., chemical characteristics, generating sources, and disposal methods).

2. Review literature for information on alkaline cleaners (e.g., current technology, chemical characteristics, and disposal methods).

3. Evaluate the economics of substituting alkaline cleaners for organic solvents.

4. Evaluate the environmental benefits of alkaline cleaners by performing a comparison analysis with organic solvents.

5. Discuss results based on research.

6. Contrast the results of this study with the previous work examining terpene-based cleaners.[25]

1.4 Mode of Technology Transfer

The findings of this research will be published in a Public Works Technical Bulletin.

Chapter 2

Background

2.1 Regulation History

The development of legislation governing the use and disposal of solvents has coincided with our increasing knowledge of environmental hazards. The first step in hazardous waste reduction was taken in 1965 with the Solid Waste Disposal Act (SWDA).[38] The act allocated money for research and technical assistance to help develop proper disposal methods for state and local agencies. In 1970, Congress realized the complexity of the problems and expanded the SWDA to form the Resource Recovery Act.[37] This law recognized the importance of sanitary landfills and encouraged process alternatives from basic disposal to conservation, recycling, and new control technology. Legislation to this date focused mainly on municipal waste (i.e., paper, glass, cans, and garbage). But as more scientific information was compiled, evidence indicated that waste generated by chemical and industrial processes could also pose a threat to the environment. As a result, Congress passed RCRA in 1976.[38] This act formed the foundation for regulation of waste generators, waste transporters, and waste management facilities.

Due to publicized disasters like Love Canal, NY, pressure was put on the Federal government to improve legislation reducing or eliminating the dangers of hazardous waste. In response to this outcry, Congress revised RCRA and passed CERCLA in 1980.[35] Under CERCLA, the generators of waste can be held responsible for corrective action and response cost. This law allows the government to step in and eliminate any actual or threatened release of hazardous waste that could have adverse effects on public health. CERCLA grants the government power to recover response costs for cleanup wastes from four classes of defendants: (1) current owners of a disposal site, (2) past owners of a disposal site, (3) generators who arrange for disposal at a site, and (4) transporters of waste to a site from which the waste is released or is threatened to be released.[35]

The 1980 revisions to RCRA implemented a base regulatory program to create standards for handling and disposing of hazardous waste. The USEPA planned to develop a program that involved cooperation between Federal and state agencies in issuing strict and comprehensive site-specific permits. To expedite the implementation of the base program, the USEPA concentrated its efforts in authorizing states. As a result, the USEPA was slow to develop and promulgate other important RCRA regulations. Due to the lack of RCRA rulemaking, Congress took a stronger role in establishing environmental legislation.

On November 8, 1984, Congress passed the Hazardous and Solid Waste Amendments (HSWA) and established over 70 statutory requirements (summarized in Table 2.1).[38] By amending RCRA, Congress declared hazardous waste reduction a national priority and became the driving force behind the program. Under HSWA, Congress set deadlines for the USEPA to enforce land disposal prohibitions (see Table 2.2). These "hammer provisions" were designed to help Congress keep the USEPA on a strict schedule. The new amendments established greater liabilities on hazardous waste for generators, treaters, and disposers. HSWA requires generators to create in-house waste minimization programs, meet predisposal treatment standards, and supply new landfills and other waste disposal facilities with additional technological controls before receiving waste. The new RCRA represents a change in national policy encouraging waste reduction, recycling, and new treatments for flammable, reactive, corrosive, and toxic waste as an alternative to landfills that now threaten air quality and vital groundwater resources.

TABLE 2.1 - SUMMARY OF KEY ISSUES ESTABLISHED BY THE HSWA[38]
• Move away from land disposal as the primary means of hazardous waste management by requiring treatment of wastes before their final disposal.
• Reduce the environmental and health risks posed by hazardous waste still managed at land disposal facilities by establishing minimum technology requirements.
• Close down facilities that cannot safely manage wastes.
• Decrease and clean up releases to the environment from waste management units by requiring facilities to take corrective action.
• Issue permits for all treatment, storage, and disposal facilities within prescribed time frames.
• Close the loopholes in the types of wastes and waste management facilities not covered under RCRA.
• Expand the universe of regulated sources by including generators of small quantities of hazardous wastes.
• Minimize the amounts of waste being produced.

2.2 Clean Air Regulations

The Montreal Protocol and U.S. Clean Air Act Amendments are examples of recent legislation passed to control harmful ozone-depleting substances. The Montreal Protocol, passed in 1987 and amended in 1990, proposed restriction of the production and consumption of ozone-depleting chemicals such as 1,1,2-trichloroethane, 1,2,2-trifluoroethane, and 1,1,1-trichloroethane.[20] The goal of this legislation is to completely phase out these chemicals by the year 2005. Besides developing deadlines for phaseout, the Montreal Protocol established a fund to help third world countries finance the incremental costs of phasing out these harmful chemicals.

TABLE 2.2 - SCHEDULE FOR LAND DISPOSAL PROHIBITIONS[35]

EFFECTIVE DATE	PROHIBITIONS
November 8, 1986	Dioxin containing wastes (F020, F021, F022, F023, F026, F027, F028) Spent solvents (F001, F002, F003, F004, F005)
July 8, 1987	California list wastes (Liquid hazardous wastes containing: free cyanides, PCBs and certain metals at or above specified concentration levels, and those liquid hazardous wastes having a pH of less than or equal to 2.0. Also, both liquid and non-liquid hazardous wastes containing halogenated organic compounds at or above specified concentration levels.)
August 8, 1988	At least one-third of all listed hazardous wastes Wastes disposed of in injection wells
November 8, 1988	Contaminated soil and debris from CERCLA Section 104 or 106 response actions and RCRA corrective actions
June 8, 1989	At least two-thirds of all listed hazardous wastes
May 8, 1990	All remaining listed hazardous wastes All characteristic listed hazardous wastes

The U.S. Clean Air Act, amended in 1990, has the same goals as the Montreal Protocol but with more stringent phaseout dates (see Table 2.3). The Clean Air Act divides the ozone-depleting substances into two categories: Class I and Class II. Class I includes all fully halogenated chlorofluorocarbons, three halons, TCA, and carbon tetrachloride. Class II substances include 33 hydrochlorofluorocarbons. Each class falls under different schedules for regulation and phaseout.

With the passage of these legislative acts, many corporations have initiated programs to find alternative solvents for their cleaning processes, thereby eliminating the problems and liabilities associated with these hazardous chemicals.

2.3 Waste Minimization

The USEPA defines waste minimization as "the elimination or reduction, to the extent feasible, of hazardous waste that is generated and would otherwise be subsequently treated, stored or disposed of."[36] the main goal of minimization is to reduce the total volume and toxicity of hazardous waste to prevent future threats to human health and the environment. Waste minimization can be accomplished through three types of activities: source reduction, recycling, and treatment (refer to Table 2.4).

When designing a waste minimization process, the hierarchy shown in Table 2.4 should be followed to achieve the best results. Source reduction is the most preferable approach. This activity is advantageous since it reduces or eliminates the generation of hazardous material at the source within a process.

The next option, recycling, involves both reuse and reclamation. This activity reduces waste volume and/or toxicity with the purpose of producing a useable material or energy stream.

The last option, treatment, reduces hazardous waste volume and/or toxicity without producing a useable material or energy stream. Although each activity can be used to achieve minimization by itself, maximum waste reduction can be accomplished by combining techniques from all three processes.

Numerous incentives for minimizing hazardous waste are listed in Table 2.5. But lack of awareness and unavailability of technical and financial resources often cause minimization concepts to be rejected. Successful waste minimization must be approached systematically.

TABLE 2.3 - 1,1,1 TRICHLOROETHANE PHASEOUT[20]

Clean Air Act	Montreal Protocol
• Freeze at 1989 levels by 1991 • Freeze at 1989 levels continues in 1992 • Reduce from 1989 levels by: 1993 - 10% 1994 - 15% 1995 - 30% 1996 - 50% 1997 - 50% 1998 - 50% 1999 - 50% 2000 - 80% 2001 - 80% 2005 - 100%	• Freeze at 1989 production and consumption levels by January 1993 • 30% reduction from 1989 levels by January 1995 • 70% reduction from 1989 levels by January 2000 • 100% reduction from 1989 levels by January 2005

TABLE 2.4 - ELEMENTS OF WASTE MINIMIZATION[19]

WASTE MINIMIZATION - Reduction to the extent feasible of hazardous waste that is generated or subsequently treated, stored, or disposed of. Includes any source reduction, recycling, or treatment activity that reduces total volume and/or toxicity of hazardous waste.

STEPS	DEFINITION	TECHNIQUES
SOURCE REDUCTION	Any activity that reduces or eliminates the generation of hazardous waste within a process. Address first.	• Better Operating Practices • Product/Material Substitution • Process Change
RECYCLING	Any activity that involves use, reuse, or reclamation of waste material. Address second.	• Processed to Recover Usable Product • Regeneration
TREATMENT	Any activity that reduces volume and/or toxicity of hazardous waste without attendant generation of a reusable material or energy stream. Address last.	• Neutralization • Precipitation • Filtration • Evaporation • Incineration

The first step, a waste minimization audit, consists of reviewing existing process operations and practices to develop a detailed set of waste minimization options. The Army has instituted waste minimization audits at many of its installations and has been successful in developing a recycling program to reclaim spent Stoddard solvent and produce a material that meets Army specifications for reuse in cleaning operations.[25] Even though this method of minimization is effective, the Army realizes that solvent waste must be stopped at the source.

TABLE 2.5 - INCENTIVES FOR WASTE MINIMIZATION

Economics
- Increased land disposal costs.
- Savings in raw material and manufacturing costs.
- Avoidance of costly alternative treatment technologies.

Regulations
- Certification of a waste minimization program on the hazardous waste manifest.
- Biennial waste minimization program reporting.
- Land disposal restrictions and bans.
- Increasing permitting requirements for waste handling and treatment.

Liability
- Potential reduction in generator liability for environmental problems at both onsite and offsite treatment, storage, and disposal facilities.
- Potential reduction in liability for worker safety.

Public Image and Environmental Concern
- Improved image in the community and among employees.
- Reduced impact on the environment.

2.4 Source Reduction

Source reduction is the first step in the hierarchy of hazardous waste minimization. Reduction can be achieved through three methods: process and equipment modification, input material changes, and improved operating and housekeeping (see Table 2.6).

Process and equipment modification involves improvements to the manufacturing process or changes in the technological process to maximize reduction in the quantity of waste generated.

Input material changes can be categorized as the replacement of hazardous materials with nonhazardous materials. Because nonhazardous materials are used, hazardous wastes are not generated.

Improved operating and housekeeping involve a wide variety of activities, as shown in Table 2.6. These activities can be summarized into three areas: logistics of materials (tracking, inventory, and monitoring), personnel awareness (education and training), and accident prevention (spills and leaks).

Source reduction precludes the need for storage, transportation, treatment, and residue disposal. As a result, liabilities associated with these processes are eliminated, and the potential for economic gain makes source reduction an attractive option in the waste minimization hierarchy.

2.5 Material Substitution

As discussed in the previous section, material substitution is an effective method of source reduction of hazardous waste. Types of "clean technologies" available as alternatives for organic and chlorinated solvents include:

- Aqueous cleaners
- Semi-aqueous cleaners
- Aliphatic hydrocarbons
- Hydrochlorofluorocarbons
- Supercritical fluids
- Carbon dioxide pellets.

TABLE 2.6 - SOURCE REDUCTION METHODS

Process and Equipment Modifications
- Redesigning or replacing equipment in order to generate less waste

Input Material Changes
- Material substitution
- Material purification
- Material selection

Improved Operating and Housekeeping Practices
- Improved material tracking and inventory practices
- Improved material usage, handling and storage
- Process and equipment monitoring
- Improved scheduling
- Recordkeeping
- Preventive maintenance
- Spill and leak prevention
- Employee education and training

This report investigates the possibility of substituting an alkaline cleaner for Stoddard solvent and 1,1,1-trichloroethane used by the U.S. Army to clean metal parts. Alkaline cleaners are aqueous-based and contain virtually no volatile organic compounds. Other advantages of alkaline cleaners are biodegradability, reduced liability, reduced disposal problems, and easing workers' exposure to solvent vapors. These properties make alkaline cleaners a favorable alternative to help eliminate the generation of hazardous waste associated with organic-based solvents.

2.6 Previous Study

A report performed in 1991 by USACERL examined the possibility of using terpene cleaners (semi-aqueous cleaner) as an alternative for organic solvents in metal cleaning operations.[25] The report analyzed all aspects of terpene cleaners including cleaning efficiency, biodegradability, economics, physical properties, and toxicity.

The results of the research showed that implementing terpene cleaner substitution for Stoddard solvent requires a site-specific study of each installation. Each facility must evaluate the cleaner's compatibility with the existing treatment process, its effects on cleaning equipment and parts, and cost for implementation. Other factors that should be considered before incorporating terpene cleaners include floor space requirements, rinsing and drying equipment, cleaning enhancements, and disposal of sludge and rinsewater. For a detailed comparison of terpene cleaners to alkaline cleaners, refer to Chapter 7.

Chapter 3

Stoddard Solvent

3.1 Stoddard Solvent Applications

The most common solvents used for metal parts cleaning at U.S. Army installations are Stoddard solvent and TCA. To evaluate solvent substitution with alkaline cleaners, a better understanding of processes and applications is required. Once these operations are defined, the alternative cleaner can be compared with the solvent currently used so the economical and environmental impacts on processes at different facilities may be evaluated.

The military specification of Stoddard solvent is PD-680. In the private sector its commercial names are drycleaning solvent, varsol (Exxon), turpentine substitute, mineral spirit, and naphtha.[7] In cold cleaning operations, Stoddard solvents are frequently used due to low cost and their suitability for the job. Cold cleaning is a surface preparation process designed to remove grease, oil, carbon, and other contaminants from parts. Cold cleaning operations can be divided into four methods of application: wipe cleaning, dip tanks, steam gun stripping, and wash station. Each application will be discussed in the following paragraphs.[19,25]

Wipe cleaning is the simplest operation. It consists of soaking a clean rag with a solvent and wiping the part clean. This method is usually associated with maintenance operations that handle parts on a single-item basis. To assure cleanliness, liberal amounts of solvent are typically used. As a result, the volume of solvent used during this procedure is hard to control. Other problems with this process are that rags must be replaced frequently, lint is left on parts, increased air emissions and fire potential due to rag drying, and dirty rags can create a serious waste disposal problem.

Dip tanks, or soak cleaning, involve soaking the parts in a large tank of cold solvent. This process is used widely in maintenance and manufacturing facilities. Small parts are usually placed in a barrel or wire-mesh basket when being cleaned, and larger parts are put on racks. Heating the tank achieves a greater degree of cleaning efficiency. Other ways of increasing efficiency are through agitation and ultrasonics. Agitation involves bubbling air into the tank to increase mixing, and ultrasonics use high frequency sound waves to produce cavitation. This causes a rapid implosion of bubbles, creating a vigorous scrubbing action on parts. All three methods are highly effective for increasing cleaning efficiency.

Steam gun stripping is often used to remove paint from metal surfaces. Solvents are fed from a storage tank to a steam gun equipped with a special valve that can adjust the mixture of solvent and steam. The part is first sprayed by a mixture of solvent and steam and then rinsed with pure steam. This operation requires large amounts of solvent, which generate contaminated rinsewater that needs to be collected and properly treated before disposal.

Wash station usually consists of a barrel equipped with a pump that circulates the solvent to provide a continuous stream of liquid used to clean parts. Dissolved material accumulates in the solvent, and solids are often removed with screens or filters. Once the solvent's cleaning efficiency is no longer acceptable, the barrel is replaced.

3.2 Generating Sources

It is estimated that over 1 million cold cleaning processes are operating in the United States today. Approximately half of those processes use a Stoddard-type solvent, which creates an annual consumption rate of more than 220,000 metric tons.[7] Manufacturing industries that use this solvent include furniture and fixtures, metal and machinery fabrication, electric and electronic equipment, transportation equipment (automobiles, trucks, ships, and aircraft), and instruments and related products. Nonmanufacturing businesses that frequently use Stoddard solvent for metal parts cleaning generally involve repair and maintenance, including automobile repair, equipment repair, and transportation maintenance. In short, most industries perform some sort of cleaning operation that in turn generates a solvent waste (see Table 3.1). In industrial processes, Stoddard solvent is generally not consumed; however, a small percentage is lost due to evaporation. Instead, the solvent is contaminated by substances removed from the metal parts it has cleaned. As the contamination level rises, it depletes the solvent's effective cleaning power until the solvent becomes "spent." Typically, the solvent can contain 30 to 40 percent fuels, oils, water, and solids before it needs to be replaced.

Numerous Army installations employ Stoddard solvent for a variety of uses. A study conducted by USACERL found 29 large military installations that generate 500 drums (27,500 gallons) of Stoddard solvent annually and approximately 124 smaller installations that annually generate 150 drums (8250 gallons) of Stoddard solvent.[7] The main source of solvent waste production tended to be around the motor pools, vehicle maintenance facilities, and aviation maintenance facilities. The following paragraphs describe each type of facility and its use of Stoddard solvent.

<u>Motor Pools and Vehicle Maintenance Facilities</u> (MPVM) typically repair and maintain tactical and nontactical vehicles. Tactical vehicles can be tracked vehicles (self-propelled howitzers, guns, mortars, and armored personnel carriers) and wheeled vehicles (cargo trucks, ambulances, truck tractors, and wreckers). Nontactical vehicles can be classified as administrative (cars, vans, trucks), engineering maintenance (trucks, bulldozers, forklifts), and grounds maintenance (tractors and mowers). Solvent sinks and spray equipment containing Stoddard solvent are used to remove oil and grease from engine parts and equipment.[6]

<u>Aviation Maintenance Facilities</u> (AMF) are used at most installations for helicopters and airplanes. Various services are performed on the aircraft, including periodic maintenance (fluids change, tuneup, etc.), engine repair, brake servicing, battery repair/servicing, exterior aircraft cleaning, and unique repairs. As with the motor pool, Stoddard solvent is used in conjunction with solvent sinks and spray equipment for cleaning oil and grease for engine parts and equipment.[6]

TABLE 3.1 - STODDARD SOLVENT WASTE GENERATION[16]

- Solvent that has become contaminated or deteriorated due to improper storage or handling.
- Solvent residues and sludges, such as tank bottoms and still bottoms.
- Solvent-contaminated industrial refuse, such as rags and filter cartridges.
- Contaminated soils or water from solvent spills.
- Dilute aqueous wastewater containing low concentrations of solvent, resulting from cleaning parts, equipment, tanks, and process lines.
- Solvents released as vapors into the atmosphere.

3.3 Chemical Properties

Stoddard solvent, which has the approximate formula of C_9H_{20}, is a member of the Aliphatic Hydrocarbon group. The solvent is manufactured by distilling crude oil at its approximate boiling range fractions and treating the product to improve odor and color stability.[11] Stoddard solvent is a blend of paraffinic, naphthenic, and aromatic hydrocarbons that are found naturally in crude oil. The proportions of these compounds present in the oil greatly affect the solvency power as well as other properties. To determine the solvency power of the compound, a test is done to determine the Kauri-Butanol value. The higher the value the more potent the solvent is for cleaning.

Two types of Stoddard solvent are presently specified by the U.S. Army, Type I and Type II (see Table 3.2). Type I can be distinguished from Type II by its low flash point (100 °F). Type II solvent, which possesses a higher flash point (140 °F), is recommended for cleaning parts at Army installations because of regulatory and safety concerns.[25]

3.4 Toxicity

In recent years, concern has grown over the short- and long-term effects of organic solvents (e.g., Stoddard solvent, TCA, etc.). This concern has prompted researchers to investigate the acute and chronic effects of the solvents when exposed to workers. Data retrieved from these epidemiological studies have shown that statistically significant chronic changes occur in peripheral nerve functions due to exposure. These symptoms tend to persist for months or years following cessation of exposure. Neurobehavioral effects in workers due to chronic exposure have also been documented. Effects include fatigue, irritability, memory loss, mood changes, and impaired intellectual function. Based on the identified adverse health effects of solvent exposure, the National Institute for Occupational Safety and Health (NIOSH) has recommended that employers use engineering controls, personal protective equipment and clothing, and reduction of exposure levels to those specified by existing standards.[33] These standards include the

TABLE 3.2 - PHYSICAL PROPERTIES OF STODDARD SOLVENT[7]

Property	Type I	Type II
Commercial reference	Stoddard	140 °F Stoddard
Appearance	Colorless liquid free of suspended matter and undissolved water.	
Flash point	100 °F	140 °F
Kauri-butanol value		
Min.	29	29
Max.	45	45
Odor	kerosene-like odor, nonresidual	
Specific Gravity		
Min.	.754	.768
Max.	.820	.820
Boiling Pt. (°F)	300	350
Vapor Pressure (mm of mercury)	<1.0	<1.0
% Volatile	100	100

recommended exposure limits (RELs), and the American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit values (TLVs) (Table 3.3).

3.5 Reactivity

Stoddard solvent is fairly stable under normal conditions, but due to the physical properties of the liquid, caution should be observed during storage and handling. Due to the solvent's low flash point, combustion of the liquid is possible and all sources of ignition should be avoided. Vapors emitted from the solvent can also ignite; therefore, areas should be well ventilated to prevent accumulation and the possibility of explosion. Stoddard solvent is not compatible with strong acids and bases, oxidizing agents, and selected amines, so contact with these materials should be avoided.[25]

3.6 Hazardous Considerations

The National Fire Protection Association (NFPA) rates Stoddard solvent as slightly hazardous with a health hazard classification of 1 (on a scale of 0 to 4; 0 being the least and 4 being the worst). Therefore, caution should be observed at all times when handling this material. The material should be stored in a cool and well-ventilated location. The containers should be tightly sealed to prevent evaporation of the solvent. Continuous contact with the solvent should be avoided; therefore, protective equipment (i.e., rubber gloves, face shield, coveralls, and an all-purpose canister mask) should be worn to protect workers from exposure. The following treatments and measures should be followed when handling this substance:[22,28,25]

Hygienic Precautions - Adequate ventilation. Prevent exposure of individuals with diseases of the central nervous system, liver, or kidneys.

Hygienic Treatment (First Aid) - If substance gets into eyes, immediately irrigate eyes with water. If chemical contacts skin, wash contaminated areas of the body with soap and water promptly. If the solvent is swallowed, immediate medical attention is required. If a large amount of the material is inhaled, move the individual to fresh air at once.

Fire Precautions (in case of outbreak) - Use dry chemical, foam, or carbon dioxide. Water spray may be an ineffective extinguishing agent, but should be used to keep fire-exposed containers cool.

Spills and Leakage - If a spill should occur, all sources of ignition should be removed from the area to prevent fire. If possible, material should be prevented from entering sewers, storm drains, other unauthorized treatment drainage systems, and natural waterways. Wearing the protective equipment mentioned above, workers can clean the solvent spill with an appropriate absorbent material.

3.7 Recycling

At many Army installations, Stoddard solvent is being recycled through distillation (onsite) and contract or leased recycling (offsite). In the distillation process, stills are used to reclaim over 4000 gallons of contaminated solvent per year. During the process, the used solvent is boiled and the vapors

TABLE 3.3 - STODDARD SOLVENT EXPOSURE LIMITS[33]

NIOSH REL	OSHA PEL	ACGIH TLV
350 mg/m^3 TWA 1800 mg/m^3 ceiling (15-min)	2900 mg/m^3 (500 ppm) 8-hr., TWA	100 ppm (525 mg/m^3) TWA 200 ppm (1050 mg/m^3) STEL

are condensed and collected in a separate container.[6] Due to the difference in boiling points between the solvent and the contaminants, the mixture can be separated, leaving the impurities in the bottom of the still. The purity of the reclaimed solvent is dependent on the level of contamination. Therefore, it is recommended that solvent wastes be segregated form oils and other wastes that might be present in the service areas. Contract or lease recycling involves using an outside contractor that periodically replaces used solvent with fresh solvent. Safety Kleen is a contractor that specializes in this type of operation. Such a system transfers responsibility for handling and disposal to an offsite company. This relieves base personnel from dealing with the waste generated from Stoddard solvent use. With an outside contractor, waste can be better contained and recycled rather than be disposed of.[6]

3.8 Disposal Options

When Stoddard-solvent waste generated during cleaning operations is nonrecyclable, proper procedures must be taken to ensure the complete disposal of the waste product. The four primary ways in which DOD installations currently handle solvent waste (incineration, fuel substitution, surface disposal, and sale) are outlined in Table 3.4.

TABLE 3.4 - DISPOSAL OPTIONS FOR STODDARD SOLVENT[7]

- INCINERATION: This method involves burning the waste solvent with air in an incinerator. In order to comply with U.S. Environmental Protection Agency and state regulations concerning air emissions, segregation of the waste from chlorinated hydrocarbons, lead and other metals, and contaminated water is required. Incineration is an attractive alternative since it destroys the waste permanently through oxidation. This method of disposal can be used with a variety of materials such as oils, greases, and other hydrocarbon products that cannot be reclaimed readily.

- FUEL SUBSTITUTION: This option is preferred over incineration because energy is obtained when the waste solvent is burned. Boilers and other firing equipment are typically used at DOD installations for this alternative. As with incineration, emission regulations must be obeyed. Therefore, no halogenated hydrocarbons should be allowed to contaminate the waste stream. Mixing the waste with regular fuels has also been cost effective with no adverse air pollution effects.

- SURFACE DISPOSAL: The disposal of Stoddard solvent by this method has been relatively ineffective. Waste solvents have been employed for dust control on roads. However, when the waste stream consists of primarily Stoddard solvent, the application tends to evaporate quickly or run off with rain, contaminating the air and water. Another alternative for disposal is using oil-consuming soil microorganisms to biodegrade the waste. This method was encouraging, except in cases where excessive rainfall occurred and runoff of hydrocarbons contaminated adjacent water sources.

- SALE: This alternative tends to be profitable and environmentally acceptable provided the buyers use appropriate reprocessing equipment. Before the solvent is sold, it must be segregated at the point of generation and labeled properly. Typical prices at some installations are $.40 per gallon of spent solvent.

Chapter 4

1,1,1-Trichloroethane

4.1 1,1,1-Trichloroethane Applications

1,1,1-trichloroethane (TCA), or Methyl Chloroform (MC), is commonly used at U.S. Army installations for metal parts cleaning in vapor degreasing operations. In the early 1970s, TCA replaced trichloroethylene as the primary solvent used in degreasing processes. Newly passed Clean Air Act regulations restricted the use of trichloroethylene due to its photochemical reactivity and resultant production of atmospheric oxidants.[4] TCA was chosen as a replacement because the solvent performance is comparable to trichloroethylene (primarily due to similar boiling points). The advantages of using TCA over trichloroethylene include a lower operating temperature necessary for cleaning that makes parts handling easier, the substantially lower photochemical reactivity of TCA, that helps maintain air quality, and the lower toxicity of TCA, making it safer to work with.

Many types of commercial vapor degreasers are available in the United States. The most common degreaser employed at Army installations is the open-top-tank vapor degreaser.[6] Other types of processes involve a conveyor system that can operate with both cold and vaporized solvents. These types of units include the cross-rod degreaser, monorail vapor degreaser, and vibra degreaser. All of these vapor-phase systems rely on hot solvent vapor condensing on the metal part as it is inserted into the degreaser. As the vapor condenses the contamination is dissolved and rinsed from the part. The contaminated solvent falls back into the degreasing tank where it is revaporized, leaving the impurities behind. To generate the vapor, heater coils in the bottom of the tank are used to bring the solvent to a boil. Being denser than air, the vapor displaces the air and creates a vapor zone. Condensers located in the top of the tank keep most of the solvent from escaping through the open top. Descriptions of these degreaser systems are discussed in the following paragraphs, and Figures 4.1 through 4.4 illustrate.*

Open Top Vapor Degreasers consist of a large tank equipped with a heating unit, cooling coils, and a water separator. The tank can be designed with a variety of heating systems that use steam, electricity, or fuel combustion to heat the solvent. These units are located in the bottom of the tank. The cooling coils are some distance below the top lip of the degreaser tank. Placing the cooling units below the top edge protects the vapor zone from disturbances caused by air movement present in the work area. The freeboard is the distance from the top of the vapor zone to the top of the tank. This distance is determined by the placement of the condenser coils and is typically 50 to 60 percent of the width of the degreaser. The water separator is used to remove the water from the condensed solvent before it returns to the degreaser tank. Troughs located below the condenser coils catch the solvent and moisture and direct it towards the separator. The water separator is a simple container that allows the water (being immiscible and less dense than the solvent) to separate from the solvent and decant from the system.[34]

Cross-Rod Degreasers are enclosed conveyer systems that help prevent solvent losses due to air movement in the work area. The unit's name comes from the cross rods that support the parts as they are conveyed through the cleaning process. The parts can be contained in a pendant basket or a tumbler as they pass through the system. The pendant basket is a simple metal basket in which parts are placed. The tumbler is a perforated cylinder that is rotated by a rack and pinion within the solvent or vapor zone. The tumbler is useful for handling small parts that require immersion or when solvent drainage from cavities is necessary.[34]

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*Figures appear at the end of the chapter.

Monorail Vapor Degreasers are widely used in industries where monorail conveyor systems prevail. These systems are enclosed to diminish solvent losses. Parts pass through the unit suspended from a chain that is attached to a monorail. These units can be automated and inserted between manufacturing operations so parts can be cleaned before moving on to the next process.

The Vibra Degreaser uses vibration to convey the parts through the vapor zone. Dirty parts are fed into a chute and fall into a pan filled with solvent. The pan is connected to a spiral elevator that is vibrated, causing the parts to move from the pan, up the spiral, and to the exit chute. As the parts move up the spiral into the vapor phase, solvent condenses on the components. As the components leave the vapor phase and exit the unit, the solvent evaporates, leaving the part dry. This type of system creates considerable noise; therefore, acoustical insulation or a noise-control booth is required.[34]

4.2 Generating Sources

TCA is used in the United States primarily as an industrial solvent for cold cleaning of metals, for vapor degreasing, and as an intermediate product in the production of 1,1 dichloroethylene.[26] At military installations, TCA is used commonly for cleaning and degreasing parts in repair, rebuilding, and finishing operations. USACERL researchers investigated waste solvent generation at military facilities within DOD. The USACERL report classified the installations as large or small based on their waste production.[8] The large facilities (approximately 29 bases) each generated 400 55-gallon drums of waste solvent annually from vapor degreasing operations. The smaller installations (approximately 124 bases) were low-volume consumers and produced a negligible amount of waste solvent annually.

TCA is typically used at U.S. Army Industrial Maintenance and Small Arms Shops (IMSS), which are responsible for maintaining everything from office machines and furniture to small arms and nuclear weapons.[6] Generally, IMSS use open top vapor degreasing for metal parts cleaning in metal-finishing and metal-working operations.

4.3 Chemical Properties

TCA, the chemical formula CH_3CCl_3, is a colorless, volatile, nonflammable liquid that possesses a sweet, ethereal odor.[26] TCA is produced by adding hydrogen chloride to 1,1dichloroethylene in the presence of a ferric chloride catalyst.[17] This solvent can be used by itself or mixed with other solvents to remove grease, paraffin, wax, and many other organic substances. TCA can be a highly unstable compound. In the presence of metallic salts, at 150 °C, TCA will decompose to form 1,1dichloroethane and hydrogen chloride. These two compounds and phosgene can also be produced when TCA is exposed to ultra-violet radiation. The biodegradability and mobility of TCA is considered moderate due to its tendency to be adsorbed by soils, increasing the soil organic carbon content. For more information about properties of TCA refer to Table 4.1.

4.4 Toxicity

TCA has been classified as moderately toxic. The concentrations at which odors are first detectable range from 16 to 400 parts per millon (ppm) depending on the sensitivity of the individual. Vapors emitted from the solvent are readily absorbed by the lungs, skin, and gastrointestinal tract.

The acute toxic effects of TCA on the human body range from mild irritation to death. At low concentrations (500 ppm), the vapors emanating from the solvent tend to irritate the eyes and mucous membranes of the respiratory tract. As the concentration increases to 900 ppm, exposure to the vapor for extended periods of time produces lightheadedness, loss of muscular coordination, equilibrium impairment, headaches, and vertigo.[13] At very high exposure levels, the solvent acts like a narcotic, depressing the central nervous system and causing hypotension, anesthesia, and coma. Liver and kidney damage has also

TABLE 4.1 - PHYSICAL PROPERTIES OF 1,1,1-TRICHLOROETHANE[8,10,28]	
Boiling Pt. @ 760 mm Hg	165°F
Specific Gravity @ 25/25°C	1.32
Vapor Density (air = 1)	4.6
Evaporation Rate	4.6
Flash point	none
Solubility (g/100g) in H_2O @ 25°C	.05
Kauri-Butanol Value	124
Vapor Pressure, mm Hg	132
Liquid Density lb/gal @ 77°F	11
% Volatile	100
Appearance	Colorless
odor	Ether-like odor

been reported where acute intoxication of the solvent was involved. Repeated contact with the liquid may produce a dry, scaly, and fissured dermatitis, due to the solvent's defatting properties.[28] If exposure to the solvent stops, the symptoms of acute poisoning will disappear and complete recovery is possible.

The chronic effects of TCA have also been investigated to determine if the solvent is a carcinogen. The symptoms produced from chronic TCA poisoning include headaches, giddiness, incoordination, and gastric upset.[13] Currently, no sufficient evidence exists linking the solvent to the production of cancer in humans. Tests conducted on laboratory animals were inconclusive because the tumor incidence in the test groups did not differ significantly from that of the control groups. TCA exposure limits are shown in Table 4.2.

4.5 Reactivity

TCA is classified as moderately reactive; however, the solvent's chemical and physical properties make it relatively unstable. When exposed to the atmosphere, TCA vapors rapidly decompose and react with hydroxyl radicals, ozone, and other atmospheric substances.[26] These reactions contribute to the catalytic degradation of the ozone layer. When boiled in the presence of water, TCA will hydrolyze and form acid byproducts that limit its effectiveness for use in certain operations. Other compounds that are

TABLE 4.2 - 1,1,1-TRICHLOROETHANE EXPOSURE LIMITS[10,28]

NIOSH REL	OSHA PEL	ACGIH TLV
350 ppm ceiling w/ 15-min. sampling period	350 ppm, TWA 450 ppm, STEL	350 ppm, TWA 450 ppm, STEL

reactive with TCA include strong caustics, strong oxidizers, and chemically active metals (e.g., aluminum, magnesium powders, sodium, potassium).[28]

4.6 Hazardous Considerations

When handling TCA, protective equipment should always be worn (i.e., gloves, apron, and goggles). Since TCA attacks natural rubber, protective equipment should be manufactured from other material such as leather, polyvinyl alcohol, or neoprene. The solvent storage area should be free from moisture and well ventilated to ensure harmful vapors do not accumulate. The following treatments and measures should be followed when handling this substance:[10,22,28]

Hygienic Precautions - Personnel who are continually exposed to the solvent should have annual physical examinations. Preclude from exposure individuals with liver or kidney disfunctions.

Hygienic Treatment (First Aid) - If the solvent contacts the skin, immediately flush with water and remove contaminated clothing. If the substance gets into the eyes, irrigate with flowing water for about 15 minutes and consult medical personnel. If the solvent is ingested, the worker should be rushed to the nearest medical facility for treatment. Do not induce vomiting. When a high concentration of solvent is inhaled, the worker should be moved into fresh air. Oxygen may be required if breathing is difficult for the individual.

Spills and Leaks - Spilled solvent should never be flushed down public sewers or into any body of water nor dumped on the ground. For small spills or leaks, simply absorb the solvent with an appropriate absorbent material. The spill can then be collected and disposed of properly. For large spills or leaks, evacuation of the contaminated area may be required. The spill should be contained immediately to avoid contamination of the surrounding area (e.g., soils, groundwater, etc.), then pumped into containers for disposal. Contaminated soil or water should be removed and treated as hazardous waste.

4.7 Recycling

Closed-loop distillation systems are commonly used at U.S. Army installations for the recovery of TCA from vapor degreasing operations. The solvent is pumped into a distillation still and heated so the TCA evaporates, leaving the impurities in the still's bottom, which is disposed of as hazardous waste. In some cases (mainly in small operations), the vapor degreaser can also be used to distill the contaminated solvent by diverting the vapor-return-to-sump line to a separate holding tank.[6] This operation is generally performed on slow workdays or during off-time hours. Filtration of the solvent is an option that does not involve recycling; however, life of the solvent in the tank can be extended and the frequency of cleaning reduced.

4.8 Disposal

When disposing of contaminated TCA (mainly from the still bottoms), the preferred option is to send waste via a permitted waste hauler to a licensed reclaimer or permitted incineration facility.[10] As mentioned earlier, under no circumstances should the solvent be flushed or dumped into a sewer, body of water, or on the ground. An appropriate container must be used to ensure no leakage before or after disposal. All disposal practices carried out must comply with Federal, state, and local laws and regulations to prevent the contamination of water and soils.[10]

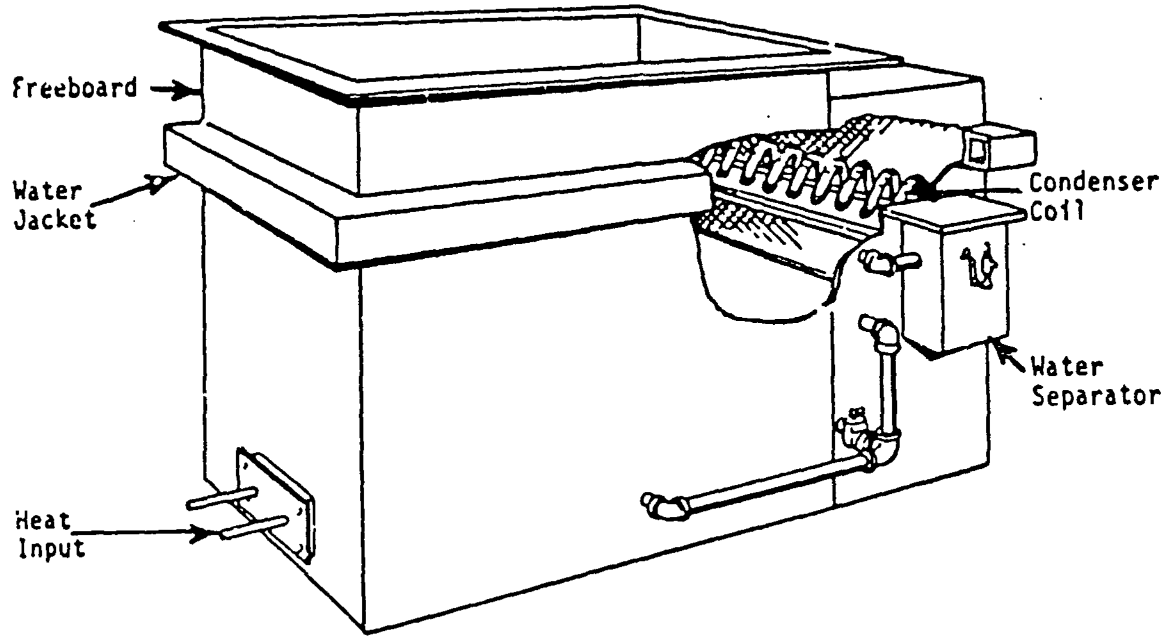


Figure 4.1. Open Top Vapor Degreaser.

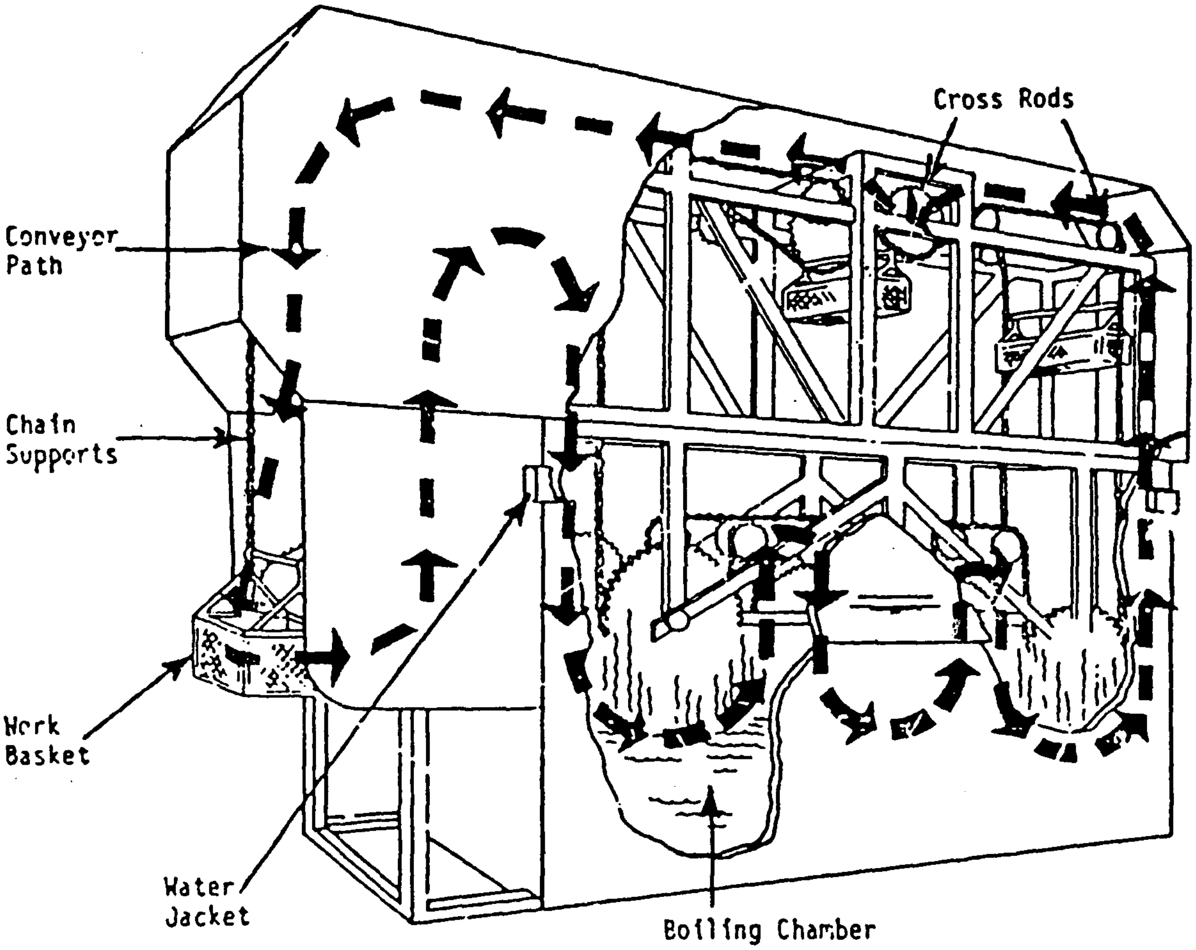


Figure 4.2. Cross-Rod Conveyorized Degreaser.

Chapter 5

Alkaline Cleaners

5.1 Alkaline Cleaner Process

Alkaline cleaning is an age-old technology used extensively throughout industry. Recently, the use of alkaline cleaners has increased due to the growing awareness of environmental and personnel safety concerns associated with chlorinated and petroleum-based solvents (i.e., TCA and Stoddard solvent). Properties associated with alkaline cleaners (i.e., nontoxic, nonvolatile, noncombustible, and biodegradable) make them an environmentally acceptable alternative for use in metal parts cleaning.

An alkaline cleaning process has three basic steps: cleaner application, rinsing, and drying (see Figure 5.1). The first step, cleaner application, can be accomplished by spray washing, agitating immersion, ultrasonic immersion, or a combination of these, depending on the site-specific situation.[31] Often a single-stage process is adequate, but when part cleanliness and appearance is paramount, multiple-stage processes should be used. The following paragraphs give a brief description of these processes.

Agitating immersion is the simplest process. It requires a large tank and some form enhancement to add the energy needed to displace and float away contaminants. Enhancements used with this process include air agitation (air diffusers), mechanical agitation (pumps and mixers), and tank heating. Soil is removed from metal parts with these enhancements by creating convection currents in the solution that increase the mass transfer of the solute into the solvent. When operating an agitating immersion bath process, the temperature ranges from 140 °F to 160 °F with typical cleaner dilutions of 1:10 or 1:20.

Ultrasonic immersion also requires a large tank for solvent storage but uses high frequency pressure waves for metal parts cleaning instead of using air or mechanical agitation. Ultrasonic cleaning works by creating turbulence through microstreaming and cavitation. Microstreaming is the creation of eddy currents through standing pressure waves.[21] The eddy currents are similar to the convective currents created in mechanical and air agitation; however, they are much more intense. Cavitation is caused by high energy sound waves pulling apart the water and leaving a cavity of vapor. When the cavity collapses, it creates high, localized temperatures and pressures.[21] Caution should be observed when designing this process to ensure that cavitation erosion of the part is not a problem and that part geometries are not ultrasonic sensitive. Operating parameters are similar to agitation immersion with bath temperatures ranging from 140 °F to 160 °F with dilutions of 1:10 or 1:20. This process is very effective for cleaning, but has high equipment and operating costs.

Spray washers clean metal parts by dispersing cleaning solution at medium to high pressures (2 to 400 psi).[20] Units available in the market today include cabinet washers, conveyorized washers, and high-pressured steam washers. The spray pressure developed in these units provide the mechanical action to break soil loose and force solution into the hard to reach places. Low-foaming detergents must be used when operating this equipment. The chemical effectiveness is not as good as immersion cleaners; however, this handicap is overcome due to the increase in mechanical agitation from the sprayers. In spray washing, the cleaner can be either hot or cold. With a cold solution, a typical concentration is 1:4, while a hot solution can have a weaker dilution of 1:10 due to the elevated temperature.

A rinse cycle is required to effectively remove any soap residue that can remain on the part. Both the ultrasonic unit and spray washer can be incorporated into a rinsing process. The spray washing units use high volumes of water sprayed at low pressures (40 to 80 psi) to effectively clean metal parts. Parts with complex configurations would require the incorporation of an ultrasonic unit to remove residues that

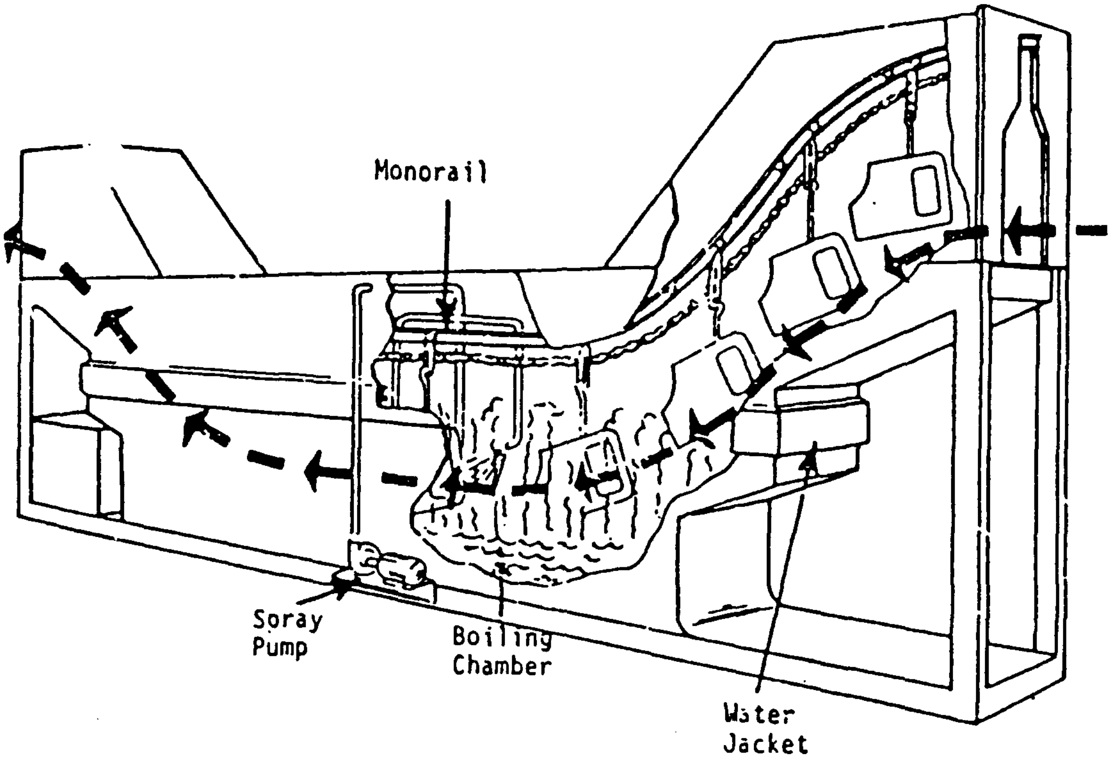


Figure 4.3. Monorail Conveyorized Degreaser.

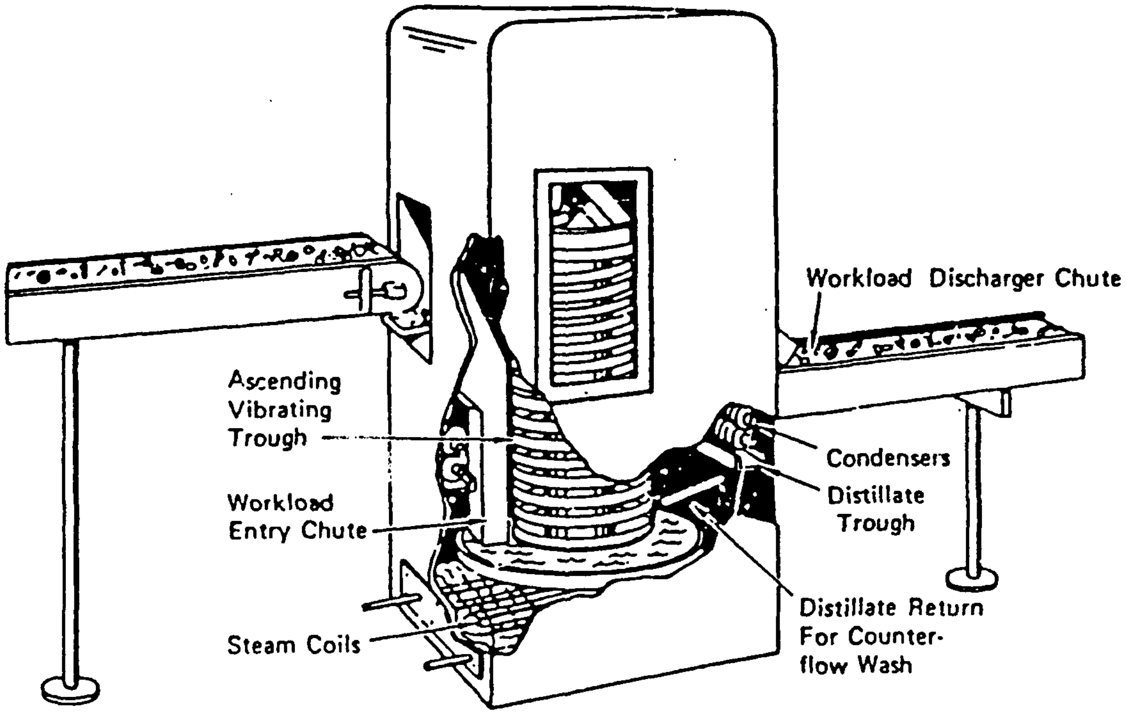


Figure 4.4. Vibra Degreaser.

are inaccessible to a spray washer. If water quality is poor, spotting can result, and it may be necessary to use deionized water depending on cleanliness requirements.

Drying is the last step in the alkaline cleaning process. Drying can be accomplished through a system using air blown at a controlled temperature and high velocity to prevent spotting and streaking on metal parts. Careful consideration should be given to the quality of air used in this system. If source air is dirty, filtration should be used to remove contaminants that might affect the integrity of the cleaned part. If corrosion is a concern, a corrosion inhibitor can be easily applied after rinsing.

Each installation's cleaning requirements will be different. It is important to choose the right cleaning process to provide quality part cleaning that equals the performance attained with solvent cleaning systems.

5.2 Chemical Properties

Alkaline cleaners for different cleaning applications vary in the type and relative concentration of their constituents. Table 5.1 lists characteristics of three typical commercial alkaline cleaners. Generally, alkaline cleaners are composed of builders and surfactants. Builders are alkalies that provide alkaline reserves to neutralize acidic soils and dispersion properties that assist in soil removal and prevent redeposition. Surfactants provide wetting and emulsification properties to wet metal surfaces, assuring intimate contact between solution and oily soils to help prevent soil redeposition.[2]

Common builders used in alkaline cleaners are sodium or potassium hydroxide. These builders give high alkaline solutions ranging from 13 to 14 pH. The cleaning ability of these alkalies are poor for non-saponifiable soils. Saponification is the reaction of any free alkali with animal or vegetable fats or with

TABLE 5.1 - PHYSICAL DATA FOR TYPICAL COMMERCIAL ALKALINE CLEANERS[1,3,18]

	HURRI-SAFE H.I.D.	**BLUE GOLD**	**3D**
Boiling Point	212°F	208°F	212°F
Vapor Density Air=1	Non-Volatile	Undetermined	Non-Volatile
Evaporation Rate	Non-Volatile	Undetermined	Undetermined
% Volatile	.005%	Not Given	Not Given
% Solubility in H_20	100%	100%	100%
Vapor Pressure	Non-Volatile	23.76 mm Hg	20 mm Hg
Specific Gravity (H_20 = 1)	1.01	1.07	1.08
Flash Point	None	None	None
Approx. Density	8.45	Not Given	Not Given
pH	12.4	13	Not Given
Appearance	Clear	Blue	Clear Blue
Odor	Non-Offensive	Solvent Odor	Pleasant Odor
Solvent Additives	2-butoxyethanol	Diethylene Gycol N-Butyl Ether	Dipropylene Glycol Methyl Ether

fatty acids, which can be obtained by hydrolysis of fats.[23] The resulting product is commonly known as soap. Therefore, these alkalies should be used when saponifiable compounds in the grease film are high. This leads to a fast reaction with the contaminant creating a high concentration of soap that improves the cleaning and soil carrying capacity of the cleaner. Strong alkaline cleaners are commonly used for iron and steel. Metals such as zinc, aluminum, copper, and brass are corroded by strong alkalies and usually are cleaned with a milder alkaline solution.

Silicates are another builder found in alkaline cleaning solutions. Typical species of silicates found in cleaners are sodium orthosilicate and sodium metasilicate. These silicates develop alkalinity through hydrolysis, a process of decomposition where the products react with water to form less soluble compounds.[2] In this case the silicates decompose to form silicic acid and free alkali. The silicic acid provides excellent solid soil dispersing and emulsification properties. The free alkali creates an alkaline reserve which acts as a buffer for the solution. The buffering property of silicates creates a reaction in which a thin film forms on some metals (i.e., aluminum, zinc, and steel). The protective coating inhibits corrosion in the alkaline solution.

Phosphates are usually found in cleaners as pyrophosphate, orthophosphate, or polyphosphates. The addition of phosphates to a cleaner is not to provide alkalinity. Instead, phosphates are added to increase the sequestering properties of the solution. In addition, phosphates have the ability to soften water in the solution and partly remove metal oxides and hydroxides from the substrate surface.[23] Although phosphates provide excellent cleaning properties, they are substituted in many products today due to environmental concern over generation of foam in rivers and streams because of high concentrations of phosphates.

Carbonates are alkaline builders found in milder alkaline products. Carbonates possess good buffering qualities that help stabilize the pH of the solution as it is cleaning. However, carbonates do not carry the same detergent qualities of the silicates (i.e., dispersion and prevention of soil redeposition).

Surfactants are typically synthetic detergents that are combined with alkalies to lower surface and interfacial tensions and increase cleaning efficiency. There are three major classes of synthetic detergents: anionic, cationic, and nonionic.[2,12,29]

- Anionic surfactants possess a negative charge on the surface active ion. The charge is localized to the hydrophilic functional group (i.e., sulfonate, sulfate, carboxylate, or phosphate) that is bonded to the hydrophobe.

- Nonionic surfactants carry no charge on the surface-active species. The water soluble parts of the molecule (usually a polyalkylether chain) have a high affinity for water. Such chains are introduced to the molecule by condensation of ethylene oxide with a reactive end group on the hydrophobe. Nonionic solubilities increase and decrease with temperature and can be raised by mixing with an anionic surfactant.

- Cationic surfactants possess a positive charge on the active species. Generally, this class of surfactant is not used in metal cleaning due to high cost, incompatibility with anionic surfactants, and ability to strongly absorb to metal surfaces. Absorption has detrimental effects on process results.

The main function of surfactants is to improve the detergency of the alkaline cleaner solution. The mixture of surfactant and alkali will depend on the type of cleaning required. Table 5.2 summarizes surfactant characteristics and how they aid in cleaning.

Complexing agents, another class of compounds, are added to alkaline cleaners to avoid undesired precipitation of scale-producing substances, eliminate staining, activate metal surfaces during the cleaning

TABLE 5.2 - SUMMARY OF SURFACTANT PROPERTIES[2]
• Acting as a liquid-solid interface, they can wet an otherwise hard-to-wet surface before cleaning.
• They can cause water to penetrate and spread underneath an oily film, for example, to lift the oil from a piece of steel and allow it to float or be removed in other ways. In such instance, they are acting at two interfaces–water-steel and water-oil.
• They can do the reverse, causing oil to penetrate and spread, which is used to assist in emulsion-cleaning operations.
• Acting as a water-oil interface, they can assist the formation of an emulsion, which may be one of two kinds. Water containing a very large number of tiny oil droplets (oil in water or O/W emulsion) or oil containing minute water droplets (water in oil or W/O emulsion). The O/W emulsion is used in emulsion-cleaning operations.
• They can penetrate through the under solid deposits ranging from scale on forgings to hard-dirt deposits, wetting both the soil and the surface to be cleaned and permitting easier separation by mechanical or chemical means.
• Acting as a water-soil interface, they can serve to keep removed soil particles from redepositing on the cleaned surface.
• Acting as a water-soil interface, they can keep soil particles in a state of maximum subdivision; that is, in a condition where they have maximum surface area so that soil stays suspended instead of clumping and settling.
• They can produce a foam to trap soil particles so that the soil is removable by skimming or similar means.

operations, and soften water.[23] Typical classes of complexing agents consist of alkanolamines, gluconates, polycarboxylic, acids, and phosphonates. Due to possible wastewater treatment problems, the stability constant of the complex formed must be taken in to account. For example, when complexing agents like ethylene diamine tetra-acetic (EDTA) are used, high concentrations of heavy-metal ions are found in the waste water. This creates problems at the treatment plant, so use of EDTA as a complexing agent should be avoided.

A wide variety of factors affect the efficiency of alkaline cleaners. For example, a typical cleaner for oil removal on steel and aluminum would contain silicates for the oil removal; tripolyphosphates for soil suspension, scale prevention, and rinsing; and synthetic detergents to improve oil penetration.[27] It is important to emphasize that the metals and soils to be cleaned for each job should be analyzed to determine the cleaner composition necessary for effective cleaning.

5.3 Toxicity

Manufacturers claim that alkaline cleaners are nontoxic. But in concentrated form, most alkaline cleaners contain a solvent (approximately 9 percent by weight) that helps the cleaner in oil emulsification. Typical solvents used are n-Butoxyethanol and Dipropylene Glycol Methyl Ether. Health hazard listed in Table 5.3 show that the toxicity of these solvents is high, but this should not be a concern in cleaning operations. In a typical operation, alkaline cleaners are diluted before use (approximately one part degreaser in eight to 20 parts water). As a result, the solvent present would make up a very small part of the bath solution (less than 0.01 percent after bath solution). Due to the solvent's low concentration, it should not pose a threat to personnel or the environment.

5.4 Reactivity

An alkaline cleaner, in concentrated form, is stable under normal conditions for storage and handling. Alkaline cleaners have no flash point, so no threat of fire or explosion exists when using or storing this material. At this time, no materials have been found that are incompatible with alkaline

TABLE 5.3 - ADDITIVE SOLVENT CHARACTERISTICS[28]

	N-BUTOXYETHANOL	DIPROPYLENE GLYCOL METHYL ETHER
TLV	25ppm	100ppm
IDLH	700ppm	Not determined
ROUTES OF ENTRY	• Inhalation • Ingestion • Skin absorbtion • Eye and skin contact	• Inhalation • Ingestion • Eye and skin contact
SYMPTOMS	• Irritation of eyes, nose and throat • Hemolysis • Hemoglobinuria	• Irritation of eyes and nose • Lightheadedness • Headaches
POINTS OF ATTACK	• Liver • Kidneys • Lymphoid system • Skin • Blood • Eyes • Respiratory system	• Respiratory system • Eyes

cleaners, and no hazardous decomposition has been recorded with this product. Also, conditions contributing to polymerization will not occur when using alkaline cleaners.[3,18]

5.5 Hazardous Considerations

Even though alkaline cleaners are nontoxic and nonreactive, care should be taken when handling these chemicals to avoid unnecessary accidents. Due to the cleaner's high alkalinity, prolonged contact with it may cause skin or eye irritation. Also, if eyes are directly contacted by the cleaner, flushing the eyes with water should neutralize any harmful effects. Alkaline cleaners are relatively innocuous substances and should not cause any harm when handled properly.

When using alkaline cleaners, typical protective equipment should be worn to prevent any health risks. Protective gloves should be worn if long exposure to this product is expected. Goggles should also be worn to protect the eyes from accidental splashing. Special ventilation should not be required due to the nonvolatile characteristics of alkaline cleaners. If excessive splashing is expected, aprons should be worn to prevent unnecessary contact with skin. If an accidental spill should happen, simply dilute the cleaner with water and clean with conventional methods. The handling of alkaline cleaners does not require special or complicated techniques and no specialized training is required. The probability of a serious accident occurring is low.

5.6 Recycling

In most cases, alkaline cleaners are not recycled. Once the solution is spent, the entire bath is flushed to a pretreatment facility and a new batch of cleaner is prepared. Recently, General Dynamics investigated ultrafiltration as a method of recycling for alkaline cleaners. The key requirement in ultrafiltration is the selection of the proper filter membrane. The membrane must be able to withstand the harsh environment (i.e., high pH, elevated temperatures, abrasive particulate matter, high hydrocarbon loading, and quantities of aggressive organic solvents). It must possess an adequate pore size capable of retaining soils in the concentrate while permitting cleaner constituent permeation.[39] General Dynamics found that ultrafiltration could remove emulsified soils and regenerate the cleaner to a quality acceptable for use.

No universal filter membrane is available for all commercial cleaners on the market. Proper testing of the filter membrane with the selected cleaner should be completed before incorporating the ultrafiltration system into the cleaning process.

5.7 Disposal Methods

Due to the biodegradability of alkaline cleaners, manufacturers claim that the cleaners can be disposed of in storm sewers or receiving waters after the solution has been neutralized at a wastewater treatment plant.

Once the cleaning solution is spent, the concentrate contains a high level of contaminants that must be removed before wastewater treatment. Generally, facilities using alkaline cleaners flush the contaminated bath solution into a sanitary sewer system specifically designed to handle the waste flow. The sewer carries the wastewater to a pretreatment facility where the solution is neutralized before going to the central wastewater treatment plant. At the pretreatment facility, the solution is run through oil and water separators and treated with chemicals to remove the organics, oils, and heavy metals suspended in the solution. After the contaminants have been removed, a diluted cleaner concentrate remains, which can be sent to the wastewater treatment plant for processing. Once the effluent is processed, it must meet the minimum USEPA concentration requirements before it is released into the environment. The removed contaminants, if classified as hazardous waste, must be treated in accordance with local, state, and Federal USEPA regulations.

5.8 Wastewater Treatment

In metal cleaning processes, generated rinsewater generally requires pretreatment before discharge into the wastewater treatment facility. Pretreatment can occur in two places, at the metal cleaning facility or at the treatment plant. Typically, pretreatment is performed at the source because contaminants are more easily removed. At a wastewater treatment facility, pollutants from many sources mix together, making separation and removal difficult and costly. The amount of contaminants and wastewater produced depends on the cleaning process. Contaminants encountered include organic materials, heavy metals, and high pH. A brief description of each pollutant is given below:[20]

Organic matter in wastewater results from oil and grease cleaned from metal parts and the chemical constituents of the cleaner. Oil and grease found in rinsewaters can be categorized as:

- Free oil - oil that rises rapidly to the surface under quiescent conditions
- Mechanical dispersions - fine oil droplets ranging in size from microns to a few millimeters in diameter that are stabilized by electrical charges or other forces but not through the influence of surface active agents
- Chemically stabilized emulsions - oil droplets similar to mechanical dispersions but with enhanced stability resulting from surface active agents at the oil and water interface
- Dissolved oil - truly soluble chemical species plus very finely divided oil droplets; generally defies removal by normal physical means

- Oil-wet solids - oil adhering to the surface of particulate material in the wastewater.

These organic materials can contribute to visual and olfactory problems, interfere with oxygen transfer, and exert both biological and chemical oxygen demands. Therefore, removal of organic material from the wastewater before discharge can reduce the load on a treatment facility.

Heavy metals in wastewater can exist in either suspension or solution. Metals in suspension generally result from chips and fines removed from the part during cleaning. Metals in solution arise from dissolved metals that are etched off as a result of the alkalinity of the solution.

High pH in wastewater streams can harm aquatic life and interfere with activated sludge treatment systems. High alkalinity is required in cleaning processes to remove oil and grease from metal surfaces. The typical pH range is from 9 to 12 and wastewater must be neutralized before discharge.

5.8.1 Pretreatment

Wastewater produced from cleaning processes can contain a number of pollutants that need to be removed before disposal. As a result, the type of treatment technology required is based on the wastewater stream and the quantity of wastewater generated. The following treatment equipment and processes are currently marketed:[20]

Gravity Separator - This equipment is used to remove oil and grease from rinsewater. This process takes advantage of the differences in the specific gravity between water and oil and grease. The wastewater is flushed to a holding tank and allowed to sit for a period of time (generally 24 hours). During this time oil and grease, being less dense than water, float to the surface and are skimmed off. This operation is low cost; however, this technique does not always remove finely divided oily or scummy material.

Ultrafiltration - This process incorporates a low pressure filter membrane for separating emulsified oils and particulate matter less than 0.2 microns in diameter. Wastewater is pumped under pressure tangentially through the membrane modules. Water, low molecular weight salts, and some surfactants pass through the membrane while emulsified oils and suspended solids are retained as concentrate. The filtered permeate can be reused or further treated before disposal. The capital and operating costs are generally high for this method; however, savings in material and disposal cost can occur when recycling of the permeate solution is possible.

Coalescing - This method works on the basic principle involving the preferential wetting of a coalescing medium by oil droplets that accumulate to form larger particles that rise to the surface. Important characteristics that the coalescing media should possess include wettability for oil and large surface areas. Typical materials used for this process are blown polypropylene, which is highly oleophilic, and monofilament line. Due to coalescing simplicity and process reliability, capital and operating cost are generally low. If emulsified oils are present in the wastewater, pretreatment is necessary before coalescing can occur.

Chemical Treatment - This pretreatment is often used to break stable oil-water emulsions. Three steps are involved in this process: (1) coagulation - breaking the emulsion, (2) flocculation - agglomeration of the tiny oil droplets to form larger particles, and (3) sedimentation - the removal of oil from the water. Breaking the emulsions involves neutralizing the repulsive forces by adding chemicals (i.e., alum, ferric chloride, etc.). Once the emulsions are broken, flocculants (high-molecular weight polymers) can be added to help in agglomeration so the oil droplets can be easily removed. The problem with this process is that the sludge produced can be classified as a hazardous waste, requiring special disposal procedures and increasing operating costs.

Carbon Adsorption - This process is highly efficient for removing dissolved organics from wastewater. An advantage of this method is that used activated carbon can be regenerated with heat and steam. This decreases the raw material cost associated with purchase of new carbon. Activated carbon columns are usually placed in series or parallel in wastewater treatment operations. For a continuous operation, a minimum of two columns is required. Using two columns provides flexibility during regeneration. As one tower is regenerated, the other can remove contaminants from the waste stream. Carbon adsorption is an economical process; the major costs are associated with the regeneration of the carbon.

Precipitation - This technique is typically used for removing heavy metals from the wastewater. Heavy metal removal consists of hydroxide precipitation followed by sedimentation. To initiate precipitation, alkaline compounds such as lime and sodium hydroxide are commonly used. A major advantage of this process is the short retention time required for settling due to metal precipitates. The disadvantages include high capital cost for installing and maintaining a clarifier and disposal costs of the hazardous sludge.

Ion-Exchange - This system removes heavy metal ions from wastewater through a reversible ion interchange process that incorporates the use of resin beds. The resin beds contain nonhazardous ions that are exchanged with the metal ion as the wastewater passes over the bed. As a result, no permanent change occurs in the bed structure. As the resin beds lose their efficiency, the system must be either regenerated or disposed of. In either case, a hazardous waste is produced and must be handled properly. Relative energy costs are low for this process.

pH Control - Generally, alkaline cleaning operation wastewaters can have pH levels ranging from 9 to 12. Water with a high pH level should be neutralized before it is discharged to a wastewater treatment plant. Typically, the addition of sulfuric or hydrochloric acid can accomplish this task. An advantage of reducing the pH is that emulsified oils are forced out of the solution, making removal less complicated and more inexpensive. The major cost of this treatment is the purchase of a mixing tank; however, operating costs are low. Figure 5.2 illustrates a conceptual design that could be used to pretreat wastewater from metal cleaning operations.

5.8.2 Treatment Processes

How will the increased use of alkaline cleaners affect the operation of treatment systems at U.S. Army installations? Presently, the U.S. Army owns and operates over 100 wastewater treatment plants across the United States. Two types of systems commonly used on U.S. bases include trickling filter and activated-sludge processes (see Figure 5.3). The effect of alkaline cleaners on the operation of these systems would depend on the specific conditions already at the plant. However, each plant would have an increase in biological oxygen demand (BOD) and high pH in the wastewater resulting from the cleaner. Ranges for operation would depend on the process in question.

Trickling filter technology has been around for more than a century and until the 1970s was the most common form of wastewater treatment in the United States. Trickling filters were so popular because of simplicity, reliability, stability, ease of operation, and energy-saving features. A trickling filter consists of a circular tank that is filled or packed with a porous medium. The medium can be large rocks or corrugated plastic containing large pores. The wastewater is evenly spread over the medium with the assistance of a rotating arm.

The trickling filter has two basic functions: (1) acts as a clarifier for solids separation and (2) removes BOD from the influent. Bacteria that grow on the medium feed on the organic matter in the wastewater and remove the BOD from the influent stream. The bacteria live at a pH level around 7; therefore, it is important that a waste stream high in pH be neutralized before entering this type of process. Wastewater high in pH would kill the bacteria and destroy the mechanism for BOD removal. High influent BOD can also upset a treatment process. If the incoming BOD is too high, the microorganisms will not be able to digest all the organic matter, causing high BOD levels in the effluent.

Activated-sludge treatment is a biological treatment process which has proven effective in treating wastewaters at many Army installations. This type of process is flexible and can be adapted to handle almost any biological waste problem. A conventional activated-sludge process generally consists of an aeration tank, clarifier, and a recycle line. The process begins with wastewater and recycled sludge entering the aeration basin at the head of the tank. Inside the tank, the wastewater and sludge are mixed by diffused or mechanical aeration for approximately 6 hours. During this time the organic matter is adsorbed, flocculated, and oxidated with the help of microorganisms in the sludge. After aeration, the sludge settles in the clarifier. From this point the sludge can either be wasted or recycled to the beginning of the treatment process. Since activated-sludge systems are biological processes, high pH and high BOD levels will result in the same detrimental effects as seen with trickling filters. High pH in the influent can kill all the bacteria, eliminating the process's ability to remove organic matter from the waste stream. Similarly, overloading the system with a high BOD wastewater can result in unacceptable levels of BOD in the effluent.

Incorporating alkaline cleaners into cleaning processes at Army installations would not cause detrimental effects in wastewater treatment operations. Typical Army wastewater treatment plants are designed to handle 3 million to 5 million gallons per day (MGD). Assuming that the average number of metal cleaning facilities (e.g., motorpools, degreasing operations, etc.) on a base is 15 and each facility uses a 500-gallon cleaning tank, the total discharge into the system would equal 7500 gallons per cleaning operation (the cleaning period runs 5 to 6 weeks). The total discharge to the system would only encompass 0.25 percent of the plant's capacity. As a result, the ability of the plant to handle the extra flow would probably not be a concern. This example assumes the worst case, that everybody dumped their bath at the same time. Generally, flow to the plant would be intermittent instead of a large surge as in the example.

High pH wastewaters would also not be a concern because the pH would be neutralized during the pretreatment process. In some cases, having high pH can be profitable. It can act as a buffer to neutralize any acid wastes that might be in the waste stream, relieving some of the pretreatment costs.

BOD levels of used alkaline cleaning solutions typically range from 10 to 100 mg/l. Maximum loading BOD loading rates for trickling filters and activated-sludge processes range from 300 to 1000 mg/l/day and 300 to 1100 mg/l/day, respectively (refer to Table 5.4). So the possibility for overload is small. However, if increased BOD does present a problem, there are other alkaline cleaners that can be substituted that do not exert a BOD. Many types of alkaline cleaners in the market are manufactured from organic constituents, inorganic constituents, and sometimes a mixture of both. Alkaline cleaners made of inorganic material exert no BOD and, therefore, would not increase the loading at the plant.

TABLE 5.4 - LOADING PARAMETERS FOR TREATMENT PROCESSES

Parameters	Activated Sludge	Trickling Filters	
		Low Rate	High Rate
Volumetric Load mg BOD$_5$/l-day	300-1100	80-400	300-1000
BOD$_5$ Removal Efficiency, %	85-95	80-85	65-90

The problems discussed above are usually resolved before a cleaner is brought into service. As mentioned previously, each plant's operating conditions are site-specific and require careful analysis before modifying existing processes.

5.9 Case Studies

Recent hazardous waste legislation has prompted organizations to study the viability of alkaline cleaners as a replacement for organic solvents. The following organizations have completed studies on the use of alkaline cleaners as a possible alternative solvent in metal cleaning processes:

1. Paducah Gaseous Diffusion Plant (Paducah, KY)
2. Idaho National Engineering Laboratory (Idaho Falls, ID)
3. General Dynamics Fort Worth Division (Fort Worth, TX)
4. U.S. Army Materiel Command: Packaging, Storage, and Containerization Center (Tobyhanna, PA).

The next four sections are brief summaries of the analytical procedures used by each of these agencies.

5.9.1 Paducah Gaseous Diffusion Plant[15]

In 1988, the Paducah Gaseous Diffusion Plant (PGDP) evaluated the performance of aqueous degreasers versus chlorinated solvents. Because of health and environmental concerns from the hazardous waste generation, degreasing operations in the plant were delineated and alternate nonhazardous solvents were evaluated for their suitability for replacing the chlorinated solvents. The comments and results of this study are summarized in Table 5.5.

In this study, eight commercial cleaners were chosen based on specific requirements dictated by PGDP. The study evaluated these cleaners focusing on cleaning efficiency, corrosion, and economics. A Kepner-Treqoe (KT) decision analysis was used to determine the three best multipurpose cleaners for the installation. The KT analysis ranked the effectiveness of the cleaner based on criteria specified during testing (e.g., cleaning efficiency, cost per use/gallon, rinsability of the cleaner, etc.). Additional testing was performed on the top three selected cleaners to determine which cleaner exhibited the best performance. Of the three, a product called Blue Gold, a heavy-duty alkaline cleaner, was chosen as an alternative degreaser for chlorinated solvents. This product had a good cleaning efficiency, no associated health risks, and was economical to use.

5.9.2 Idaho National Engineering Laboratory[21]

A program developed by the U.S. Air Force Engineering and Services Center was used to study biodegradable cleaners as an alternative to halogenated and nonhalogenated solvents currently being used by the Air Force. The purpose of the program was to:

- Identify which solvents presently being used can be replaced with biodegradable solvents
- Identify the biodegradable solvents that can be used
- Develop procedures and methods for their use
- Develop procedures for future testing.

Tests were conducted by EG&G Idaho, Inc. scientists and engineers of the Idaho National Engineering Laboratory.

The program was divided into three phases. Phase one involved the screening of numerous commercial solvents selected for testing. The screening process was based on four subtasks: biodegradability, solubility, cleaning efficiency, and corrosion testing. The products that passed these criteria proceeded to phase two.

Phase two involved more extensive testing of the selected commercial solvents. Testing consisted of human toxicity studies, biological acclimation, cleaning enhancement testing, solvent performance, and extended corrosion tests.

Phase three, the final step, consisted of full-scale testing on the remaining solvents. Out of 200 products, only four cleaners reached phase three, and two of those solvents were alkaline cleaners. This study was completed in May 1991 and the comments and results are summarized in Table 5.6.

5.9.3 General Dynamics Fort Worth Division[39]

General Dynamics, in conjunction with the U.S Air Force, developed a project to identify alternative cleaning methods to replace the organic solvents currently being employed. Technical issues of concern included substrate compatibility, corrosion, maintenance of downstream process integrity, surface coating compatibility, and limitations of process time and temperature. The project was divided into five phases:

Phase I - Substrate, Soil, and Cleaner Characterization
Phase II - Cleaner Evaluation/Optimization
Phase III - Material Compatibility and Performance
Phase IV - Pilot-Scale Testing and Factory Evaluation
Phase V - Cleaner Regeneration/Recycle

From the many products tested, three commercially available alkaline immersion cleaners qualified as effective substitutes for halogenated solvent degreasing. The results and recommendations of this report are summarized in Table 5.7.

5.9.4 U.S. Army Materiel Command[32]

In August 1988, the U.S. Army Materiel Command, at the request of the Defense Logistics Agency, initiated a program to evaluate the feasibility of substituting water-based commercial alkaline cleaners for Stoddard solvent and TCA. Tests were performed to determine the compatibility, corrositivity, and cleaning efficiency of alkaline cleaners. The results and recommendations of this study are presented in Table 5.8

TABLE 5.5 - PADUCAH GASEOUS DIFFUSION PLANT STUDY OF ALKALINE CLEANERS[15]

EVALUATIONS	COMMENTS AND RESULTS
Biodegradability	This report recommends further investigation into the disposal of alkaline cleaners to ensure the product is completely biodegradable.
Cleaning Efficiency	The tests showed that alkaline cleaners were comparable and in some cases better than chlorinated solvents.
Cleaning Enhancements	Ultrasonics and air agitation were used to remove the heavier greases more effectively.
Corrositivity	All cleaners exhibited acceptable corrosion rates at room temperature. At elevated temperatures, the corrosion rate for copper compounds were three to five times faster.
Dilution Rates (for Blue Gold)	light oils 20:1 (pH 12.1) heavier soils 10:1 (pH 12.2)
Operating Temperatures	For ultrasonics and immersion cleaning, the recommended temperature is 140°F.
Combustibility	The aqueous alkaline cleaners had no flash point.
Rinsing Requirements	Parts cleaned with degreasers were rinsed with cold tap water and air-dried with plant air.
Disposal	The spent solution required pretreatment before going to a waste water treatment plant for processing. Studies on the recycling of the cleaner are being investigated.
Economics	Analysis showed the use of alkaline cleaners is economical. The cost of using Blue Gold at a 20:1 dilution was $0.388 per gallon.
Overall Recommendation	PGDP chose Blue Gold, an alkaline cleaner, as a replacement for the existing chlorinated solvent at the plant.

TABLE 5.6 - IDAHO NATIONAL ENGINEERING LABORATORY ALKALINE CLEANER RESULTS[21]

EVALUATIONS	COMMENTS AND RESULTS
Cleaning Enhancements	Due to the inner surfaces, notches, and crevices inherent in parts, enhancements are required to achieve efficient cleaning.
Ultrasonics	Tests showed that ultrasonics can achieve good cleaning results. However, costs increase significantly when this enhancement is applied to large tanks.
Agitation	The use of an impinger, turbo, or pump system can achieve similar results (compared to ultrasonics) with less cost for larger systems.
Rinsing Requirements	Rinsing was required to remove residual soils from the part. Either fresh solvent or water can be used, depending on the application.
Drying Requirements	Tests showed the maximum drying time to be 30 minutes. If flash corrosion is a problem, dryers can be installed to decrease drying times.
Corrositivity	Most metals exhibited minimal corrosion. Aluminum and magnesium tended to corrode the greatest in most cases.
Solution Life Expectancy	Dependent on cleaners' formulation and soil loading rate.
Biodegradability	The results from an 8-day jar test showed that the organisms were able to biodegrade the solvents used in phase two.
Biological Acclimation	Most of the solvents tended either to float or disperse the sludge bed during the 21-day test. As a result, the system had a hard time acclimating to the solvent. Fremont 776 (an alkaline cleaner) did not have any adverse effect on the sludge and did not upset the system.
Full Scale Testing	Large-scale tests showed that alkaline cleaners can be used effectively and economically. The addition of cleaning enhancements would be beneficial in reducing the overall cleaning cycle time.

TABLE 5.7 - GENERAL DYNAMICS STUDY OF THREE REGENERABLE AQUEOUS CLEANERS[39]

EVALUATIONS	COMMENTS AND RESULTS
Cleaning Efficiency	The alkaline degreasers removed most soils efficiently; however, the cleaners proved ineffective in removing the high molecular weight soil called "Cosmolene."
Cleaning Enhancements	Research indicates the cleaning properties of a given alkaline cleaner are influenced by thermal, chemical and mechanical energy. Manipulation of these properties can increase a cleaner's performance.
Ultrasonics	Proved useful in removing higher molecular weight soils and cleaning parts with complex geometrics. The use of this enhancement reduces temperature and concentration requirements. Applications are limited in size and are sensitive to soil loading.
Air Agitation	Difficulty in maintaining uniform air impingement on the panel surface. In some cases, excessive foaming was exhibited.
Corrositivity	All metals tested were compatible with aqueous alkaline cleaners. Steel alloy D6AC was susceptible to oxidation (flash rusting) when exposed to air during the process.
Corrosion Protection	Three out of four cleaners passed all tests according to military specifications.
Structural Adhesion	The cleaners exceeded the specifications in all but two cases. Further investigation showed the integrity between the cleaned surface and bonding material was maintained, indicating failure within the adhesive material.
Regeneration and Recycling	Cleaner regeneration was deemed feasible with a specific ceramic ultrafiltration membrane. However, only one cleaner was found to be compatible with the filtration system. The other cleaners either lost their glycol ether constituent or could not be regenerated.

TABLE 5.8 - U.S. ARMY MATERIEL COMMAND EVALUATION OF ALKALINE CLEANERS[32]	
EVALUATIONS	**COMMENTS AND RESULTS**
Corrosion Tests	These tests evaluated the use of alkaline cleaners in both hot and cold applications. The metals tested included aluminum, brass, cadmium, magnesium, copper, zinc, and steel. Almost all the metals tested showed no signs of corrosion. The metals that were effected by the cleaner were magnesium, brass, and cadmium.
Cleaning Efficiency	Six various soil compounds were used to test the cleaning efficiency of the cold alkaline degreaser and the hot alkaline immersion degreaser. The cleaning times are as follows: • Aircraft and Instrument Grease (MIL-G-3278) Cold Degreaser: 5-10 min. Hot Degreaser: 1-2 min. Organic Solvents: 1 min. • Texaco Uni-Temp Grease Cold Degreaser: 10 min. Hot Degreaser: 1-2 min. Organic Solvents: 1 min. • Aircraft and Instrument Grease (MIL-G-23827A) Cold Degreaser: 10-15 min. Hot Degreaser: 5 min. Organic Solvent: 5 min. • Automotive and Artillery Grease (MIL-G-109248) Cold Degreaser: 15-20 min. Hot Degreaser: 5-10 min. Organic Solvents: 5 min. • Corrosion Preventative Compound (MIL-C11796B) Cold Degreaser: 1-2 hours Hot Degreaser: 10 min. Organic Solvents: 30 min. • WTR Grease, Aircraft (MIL-G-81322B) Cold Degreaser: Could not remove grease Hot Degreaser: Could not remove grease Organic Solvents: 1/2-1 hour
Results	This report considers employing alkaline cleaners for light to medium oils and greases. However, the report does not recommend the use of alkaline cleaners for heavy greases and oils in MIL-P-116 cleaning applications.

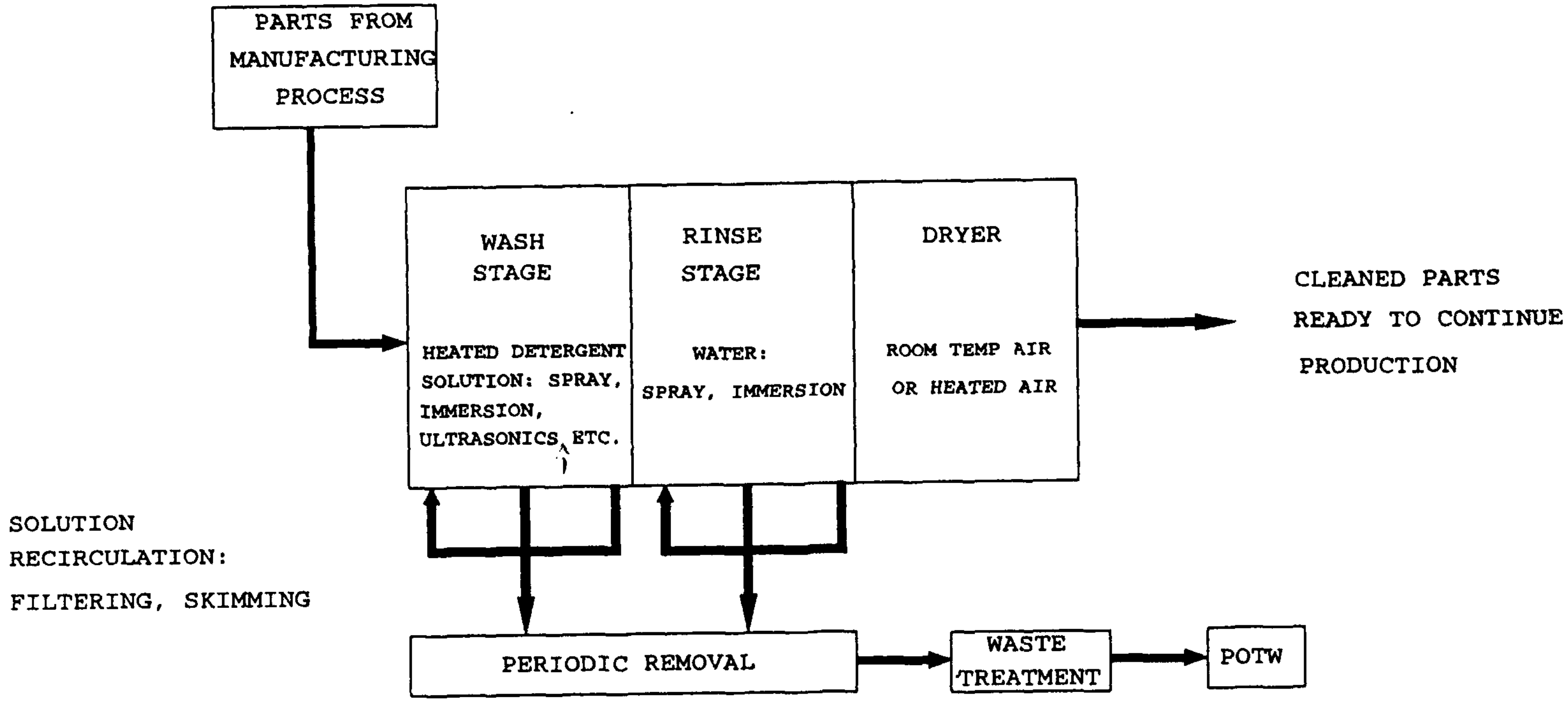


Figure 5.1. Alkaline Cleaning Process Configuration.[20]

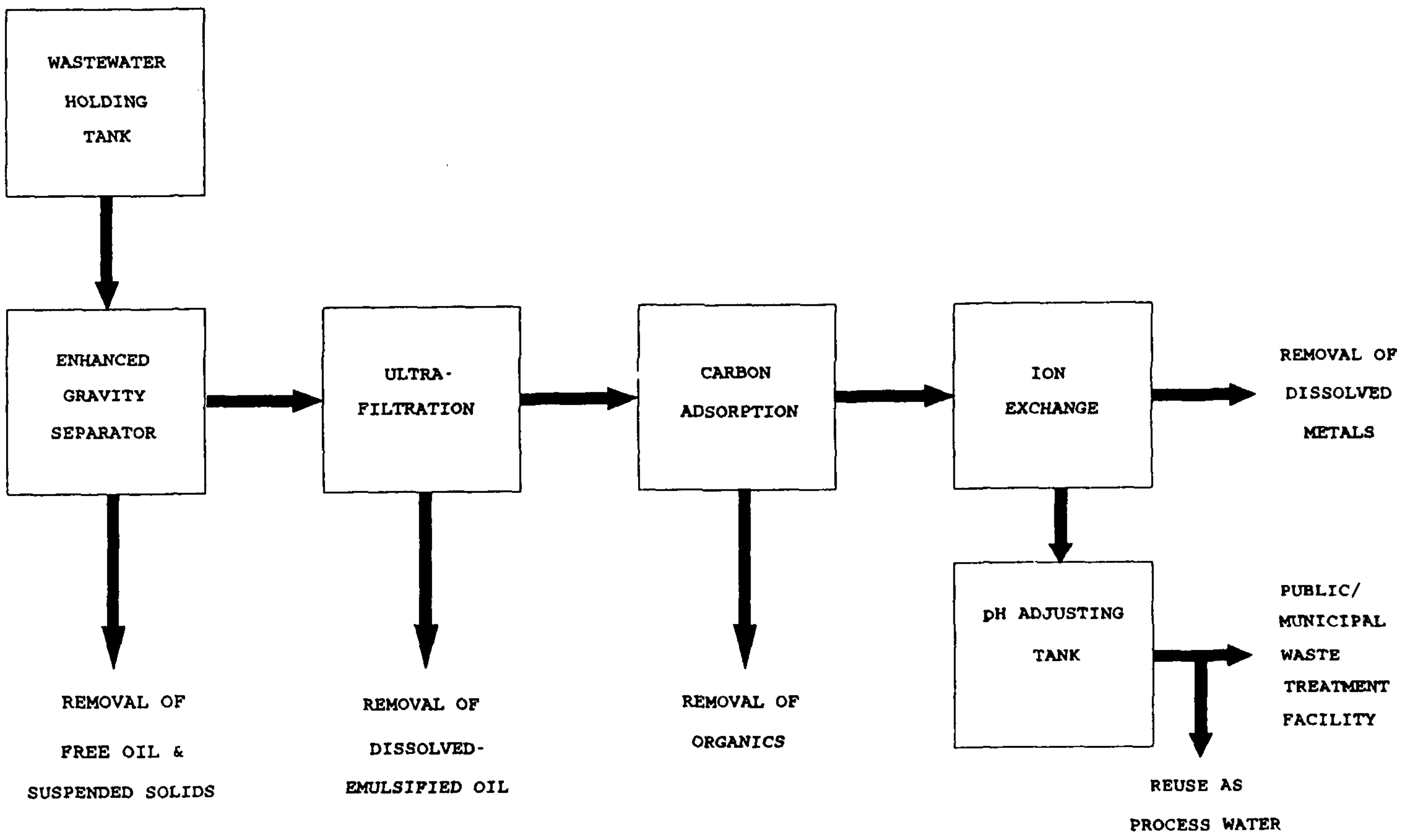
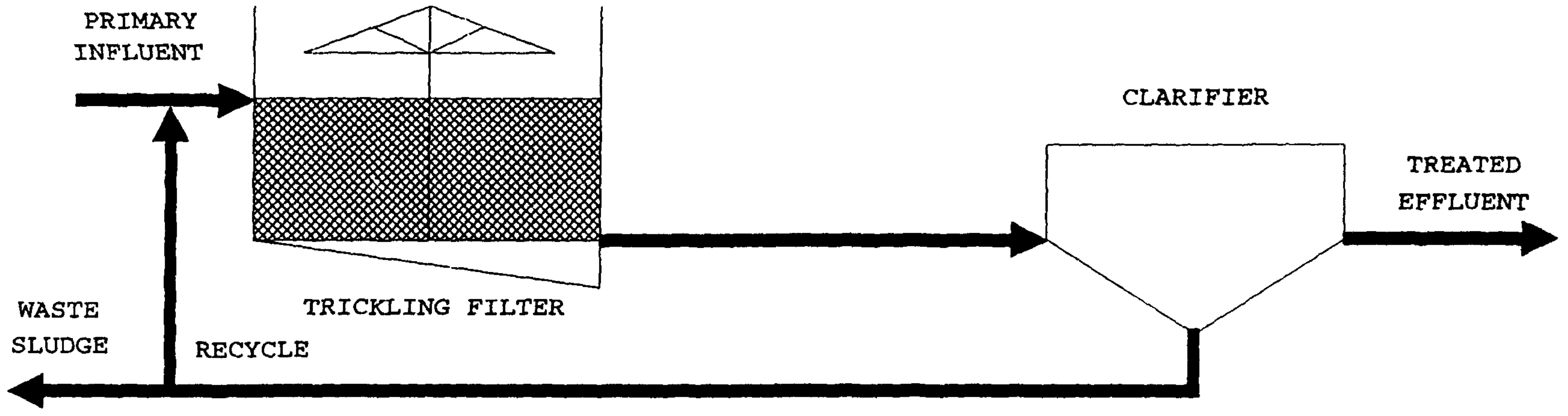
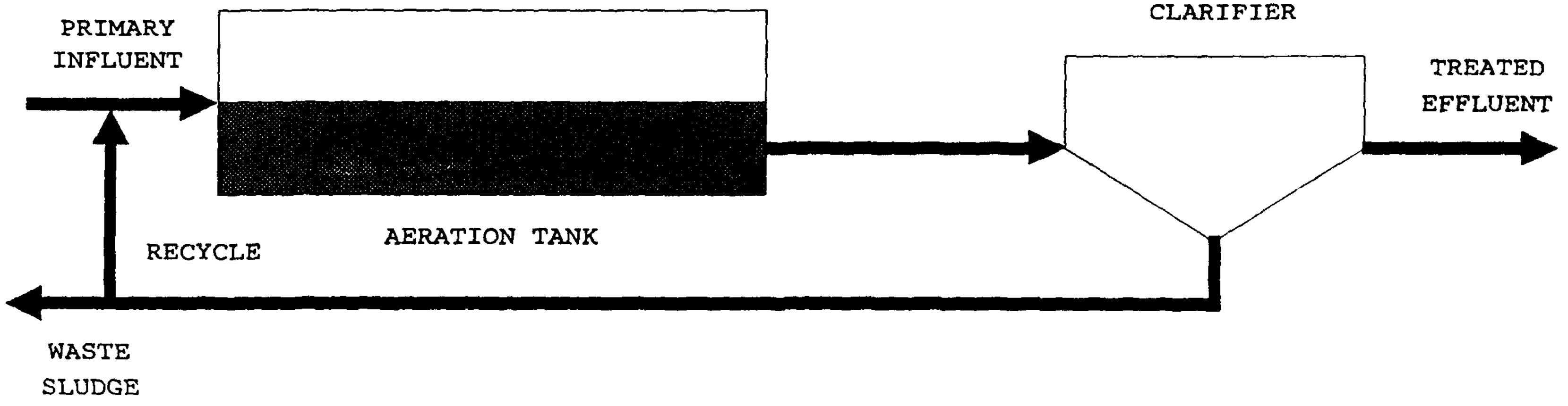


Figure 5.2. Conceptual Wastewater Pretreatment Process.[20]



TRICKLING FILTER PROCESS



ACTIVATED SLUDGE PROCESS

Figure 5.3. Wastewater Treatment Processes.

Chapter 6

Economic Analysis

6.1 Background

In July 1987, the Army developed a hazardous waste minimization program that established a goal of reducing the waste generated at its installations by 50 percent by 1992.

To simplify comparison of the economics of different waste minimization schemes, USACERL developed a program called CERL Economic Analysis for Minimizing Hazardous Waste (CEAMHW).[5] This program allows a cost-benefit analysis to be performed on various waste minimization alternatives by comparing the life-cycle cost to the cost of current operating practices. The advantage of this program is that it gives installation managers a tool to analyze multiple minimization alternatives in a short time and generate analysis documentation that can be used to help obtain funding for specific waste minimization projects.

With CEAMHW, an economic evaluation was initiated to investigate the feasibility of substituting an aqueous-based alkaline cleaner for solvents currently being used (Stoddard solvent and TCA). In this analysis, Stoddard solvent was purchased through an off-site, closed-loop recycling contract. This is a common practice at many installations for the convenience of handling and disposal. However, even though an outside contractor handles the disposal, the Army, as the primary generator, is not free from the liabilities associated with the hazardous waste. In the TCA model, the solvent was recovered and reused with the help of a distillation unit. The advantage of these units are that most processes are highly automated and require only minimal operator attention. The alkaline cleaner chosen for analysis as an alternative for the organic solvents was called Hurri-Safe. In the analysis, the alkaline cleaner was compared at two dilution rates, 3:1 and 10:1, in four enhancement options. Graphs of these comparisons are shown in Figures 6.1 through 6.4. The dilution rates were recommended by the manufacturer for cleaning heavy oils and light oils, respectively. The following is a description of the four options:

Option 1 - The conversion of an existing vapor degreaser to an alkaline cleaner tank with air agitation and oil skimming. Typical cost: $1,800.

Option 2 - Installation of a new alkaline cleaning tank with air agitation and oil skimming. Typical cost: $6,000 (1000 gallon tank).

Option 3 - Installation of a spray washing unit. Typical cost for a large capacity machine: $18,000.

Option 4 - Installation of a new alkaline cleaning tank with ultrasonic cleaning. Typical cost: $28,000.

Also considered during the analysis on alkaline cleaners was the cost of disposing the contaminants in the cleaner (e.g., oil, grease, etc.). The contaminants were classified either as hazardous or nonhazardous waste. The reason for the distinctions is due to the variance in state regulations on the classification of hazardous waste. The disposal of hazardous and nonhazardous contaminants is accounted in the economic model, which creates a more accurate analysis.

6.2 Economic Model Flow

This section examines the economic model to provide a better understanding of how the program flow functions. This summary establishes a process for assaying a problem using the CEAMHW program to determine the most economical solution by following steps:[5]

1. Choose a Waste Stream - Select the most appropriate waste stream from the six wastes listed: solvents, paint stripping, metal plating, industrial waste treatment plant sludges, used oils, and batteries. If none of these apply, the general model should be used.

2. Assumptions Window - Before any costs are entered or calculated, the defaults option in the file menu should be selected. This section will bring up the default windows so the user can review and verify equipment costs, discount rates, or adjustment percentages. These values are used for calculations later in the program. Therefore, the more accurate the defaults are, the better the model will be.

3. Choose a File - After the defaults have been reviewed, a work file can be opened. The file menu lists the files present and the new problem option. One option must be selected.

4. Define Problem - After a work file has been chosen, a menu appears that includes: problem information, comparisons, and three minimization techniques—source reduction, recovery/reuse, and treatment. Problem information should be chosen first, which allows entry of data specific to the waste stream.

5. Input Alternatives - Once the problem information has been entered, an appropriate minimization technique should be selected. This is generally accompanied with input into a alternative-specific information window consisting of two pages of information on the characteristics of the minimization technique chosen.

6. Enter Costs - Along with the alternative information, three costs are listed that may apply to the specific technique selected. The costs listed include; research and development, investments (yearly investment costs, major replacement costs, and terminal value), and operation and maintenance. Values should be entered into these costs if they apply.

7. Totals - After all cost information has been entered, the totals screen can be viewed and the alternative's cost by year will be shown. The display will include yearly present values for the chosen alternative for each year of the project's life.

8. Comparison - This function allows comparison of two minimization alternatives and a determination of which alternative is more feasible.

9. Printing - This program allows generation of documentation on all analyzed alternatives and will print the information in report format.

10. Saving and Exiting - Before exiting the model, the program will ask if the data needs to saved. It would be advantageous to save all data so adjustments can be made at a later time if needed.

6.3 Model Assumptions

The assumptions for the economic model are classified as general and solvent-specific. For a description of general assumptions refer to Table 6.1. The assumptions for each solvent are examined in the following discussion.

- **Stoddard Solvent Assumptions**

1. A full-service contracting option was incorporated in the Stoddard solvent model. Safety-Kleen, a nationwide full-service contractor, supplied cost estimates for this type of operation.
2. Three part-washing units were used.
3. The contractor was responsible for servicing the part-washing units 13 times a year.
4. The installation cost for each unit was quoted as \$30.
5. The average price per gallon of solvent was estimated at \$4.
6. No onpost labor was required to handle solvents. The contractor was responsible for handling and disposal.
7. Raw and replacement material costs were calculated based on the estimated contract price for Safety-Kleen services. The procedure for computation was to multiply the average price per gallon for Safety-Clean services (for a solvent similar in makeup to PD-680) by the installation's solvent usage/initial need (in gallons per year).

TABLE 6.1 - GENERAL ASSUMPTIONS[5]

Economic Life:

For this model an economic life of 10 years was chosen for each alternative. This coincides with Department of Defense (DOD) criteria as a default parameter.

Research and Development:

R&D costs usually involve expenditures for the development and testing of a process before it proceeds to production. In this analysis, it was assumed that existing technology will be implemented, making R&D costs equal zero.

Nonrecurring Costs:

Refers to costs that are incurred on a one-time basis. For this model a 1-year time schedule was selected for all options.

Recurring cost:

Refers to expenses that occur on a periodic basis throughout the project's economic life. The recurring cost occur at the beginning of year two, which would be the year immediately following any investment costs.

Escalation Rates:

An annual escalation rate of 4 percent was applied to operation and maintenance to account for yearly inflation.

Logistics and Procurement:

This encompasses initial nonrecurring costs of local procurement, accounting, legal fees, medical, police, fire, and any other services included in the acquisition of equipment and installation. In the model, the default value of 7 percent was used for all options.

Contingencies:

A value of 10 percent of the total equipment costs was used in the model. This is a catch-all category to provide a safe margin of error in estimating nonrecurring costs.

8. The costs associated with maintenance and repair were zero with the full-service contracting option.

9. Liability costs in the model cover possible onsite spills, cleanups, and legal claims. Therefore, a value of $0.01 per gallon of solvent used was assumed in the full-service contracting scenario.

10. Disposal costs were accounted for in the initial fees. As a result, zero was imputed into the model for the annual cost.

11. The costs for sampling and testing were also zero. Since the part-washing units are serviced regularly, sampling and testing of the solvent is unnecessary.

12. Costs for transportation and storage were zero for this option. These tasks are the sole responsibility of the full-service contractor.

13. The annual costs for logistics and procurement were estimated to be 3 percent of the total contract costs. These costs encompass annual preparation, review of bid schedules, contract preparation, and supervision.

14. Solvent losses due to evaporation were estimated at 20 percent. Losses were primarily due to bad operating practices such as open lids, dragout, and spillage.

15. Labor required from onpost personnel for collecting and distributing solvent equaled zero.

- **1,1,1-Trichloroethane Assumptions**

1. Recovery and reuse with a solvent distillation system was the alternative chosen for comparison with alkaline cleaners. These units are commonly used at many installations as a source of waste minimization.

2. The number of units used was assumed to be one.

3. The desired still backup capacity was set at 10 percent.

4. The size of the distillation unit depended on the amount of solvent used annually. With inputs less than 1000 gallons, the program would use a 15-gallon still. With flows greater than 1000, it would jump to a 55-gallon still.

5. Equipment costs for a 15-gallon still were assumed to be $13,900, and costs for the 55-gallon were assumed to be $25,400.

6. Site preparation and installation costs, including piping, electrical work, equipment installation, and engineering and supervisory fees were estimated at 10 percent of the total equipment cost.

7. A startup cost that covered the initial solvent expense was assumed. The cost was calculated by multiplying the current solvent usage by the solvent price per gallon ($4.89).

8. Raw materials and replacement costs were determined by taking the amount of solvent lost during usage (30 percent) plus the amount lost during distillation (7.5 percent) and multiplying

that value by the price of the solvent per gallon. This would be the cost of replacement with new material.

9. Total man hours required to operate the machinery was automatically accounted for in the model based on annual solvent usage. The man hours varied from 102 to 140.

10. Maintenance and repair costs were estimated at five percent of the equipment costs.

11. Liability costs for solvent distillation were estimated at $0.07 per gallon of waste (still bottoms/sludges).

12. The disposal cost for waste generated during the distillation process was assumed to be $1.45 per gallon of waste.

13. The model approximated the expense for sampling and testing during operation, at three percent of direct labor costs.

14. Transportation and storage of hazardous waste generate was estimated at $0.33 per gallon. The appraisal includes labor, machinery, and warehousing costs.

15. The model assumed the logistics and procurement expenses associated with recurring costs was 1.6 percent of the total costs for personnel, replacement materials, maintenance and repair, sampling and testing, disposal, liability, and transportation and storage.

- **Alkaline Cleaner Assumptions**

1. The price of Hurri-Safe was quoted by the manufacturer as $11.50 per gallon, in concentrated form. When used at a 10:1 dilution, the cost per gallon reduced to $1.15 ($11.50 divided by 10) and at a 3:1 dilution the cost reduced to $3.83 per gallon.

2. The number of cleaning units used for each option was assumed to be one.

3. Site preparation, equipment installation, engineering and supervisory fees were estimated at 15 percent of total equipment costs.

4. Total man hours per year required to operate each option was estimated at 140. This includes time required to prepare a fresh batch of cleaner solution, sampling, and testing. The wage rate was $11 per hour.

5. Raw and replacement material costs were calculated by multiplying the usage rate (gal/yr) by the cost of the cleaner ($/gal). Alkaline cleaners are nonvolatile so cleaner evaporation is not a problem. However, the water in the solution will evaporate and must be added periodically to maintain cleaner concentration.

6. Maintenance and repair was estimated at five percent of the equipment cost subtotal.

7. Due to the nonhazardous nature of alkaline cleaners the liability costs are low ($0.001/gal).

8. The disposal cost for the alkaline cleaner was zero, assuming that the cleaner can be discharged, after pretreatment, into the wastewater treatment system. However, a cost is associated with the oil and grease captured by the cleaner. The production rate of

contaminants is based on the loading of the system. The model estimates that 50 gallons of waste was generated every 4 weeks, giving a total of 650 gallons per year. Hazardous and nonhazardous classifications were examined in the model. Cost for disposal of contaminants were $0.35 and $0.05 per gallon, respectively.

9. No costs were associated with the transport and storage of alkaline cleaners. There is a small charge for transport and storage of oils and greases collected from the alkaline cleaning processes. Similarly, both classifications, hazardous and nonhazardous, were analyzed. The price associated with hazardous waste was $0.33 per gallon and the cost for nonhazardous was $0.008 per gallon.

10. The model assumed the logistics and procurement expenses associated with recurring costs was 1.6 percent of total cost for personnel, replacement materials, maintenance and repair, sampling and testing, disposal, liability, and transportation and storage.

11. No additional fees were considered for the construction of new storage facilities, assuming the preexisting structures on the installation were adequate.

6.4 Analysis Results

With the assumptions discussed in the previous section, an analysis was performed comparing Stoddard solvent and TCA to the alkaline cleaner Hurri-Safe. Each option for the alkaline cleaner was examined at five different solvent-use rates (1000 to 5000 gal/yr), and a cost (total net present value) was calculated for each case. The data generated by the CEAMHW model has been plotted in Figures 6.1 through 6.4. Comparisons of each option's economic feasibility to the organic solvents are discussed in the following paragraphs.

The first option, conversion of an existing vapor degreaser, was the mo favorable option due to its low startup costs. At a 10:1 dilution rate, savings in costs can be incurred at every solvent use rate. However, at a dilution rate of 3:1, a cost savings can only be achieved at the higher use rates (3000 to 5000), which results in a longer payback period. The feasibility of incorporating this option into a cleaning process depends on the condition of the existing tank. If the tank is in good condition, this alternative would be very cost effective. If the tank is in poor condition, this option would not be feasible, and a new tank would be required.

The second option, incorporation of a new tank, was also favorable at a dilution rate of 10:1. At a 3:1 dilution, the option was only cost effective at a high solvent use rate (5000) when compared to Stoddard solvent. When compared to TCA, cost savings can be obtained at any rate. It can be concluded from the analysis that this option is economically feasible; however, long payback periods will result when cleaner is used at high concentrations.

Option number three, installation of a spray washing unit, was competitive with the organic solvents at low cleaner concentrations. This alternative incurred savings over the majority of use rates tested for both the hazardous and nonhazardous waste generation cases. At the higher cleaner concentrations (3:1), this alternative became infeasible due to the process's high initial cost and operating expenses. As a result, no significant savings were incurred over the entire range of usage rates. To quantify the affordability of this cleaning alternative, the process characteristics should be discussed. An advantage of these units is their ability to obtain high agitation and turbulence for soil removal. Because of these characteristics, high cleaner concentrations are not required for the process to obtain high cleaning efficiencies. This decrease in operating cost helps make this alternative economically favorable.

The fourth option consists of using an ultrasonic cleaning unit as an alternative cleaning process. The results of this option are similar to option three. At lower concentrations, savings can only be achieved at higher use rates (3000 to 5000) due to the large initial investment, which increases the payback period. Alternatively, at higher cleaner concentrations, the use of this option becomes infeasible. As mentioned previously, an important factor in determining the economic feasibility of these high priced options is their ability to clean at lower cleaner dilutions. The ultrasonic unit can obtain very high cleaning efficiencies due to the high turbulence created by cavitation and microstreaming. This high energy input into the system allows for the use of weaker cleaner dilutions in the cleaning process. The net result is an affordable alternative for cleaning metal parts.

6.5 Case Studies

Cost-benefit analyses are performed by many corporations to determine the economic feasibility of a proposed product. The following organizations have completed economic studies focusing on the feasibility of substituting alkaline cleaners for organic solvents being used in cleaning operations:

- The Naval Aviation Depot at North Island
- Aero Precision Engineering Corporation
- Vandenberg Air Force Base.

The following sections give a brief summary of the results of the cost-benefit analyses performed by these agencies.

6.5.1 Naval Aviation Depot at North Island, CA[40]

The Naval Aviation Depot (NADEP) uses 18 solvent vapor degreasers at its facility for cleaning oils and oily contaminants from aircraft components. Recently, NADEP evaluated the feasibility of replacing the vapor degreasers with a high pressure spray washer that uses a water-based alkaline cleaner. When tested, the spray washer effectively degreased landing gear components and ordnance components. Ultraviolet light and water break-free evaluations were also acceptable and, in many cases superior, to vapor degreasers. Based on results from the comparison study and the economic analysis (see Table 6.2) it was determined that incorporation of the spray washer system would benefit NADEP in the following ways: Water consumption would be reduced annually. savings would be realized due to the decrease in costs for procurement/disposal and waste generation, a safer work environment would enhance productivity, and fewer man hours would be required to operate the process, making the system more efficient.

6.5.2 Aero Precision Engineering Corporation[30]

Aero Precision Engineering Corporation is a small company in St. Paul Park, MN, that produces precision parts for industry. To reduce hazardous waste generation, the company initiated a program to look at nonhazardous degreasers for its metal cleaning operations. Selection guidelines require that the alternative cleaning method:

- is safe for employees and the environment
- is cost effective
- does not damage delicate parts nor lead to rusting of steel parts
- meets current cleanliness specifications.

Based on these criteria, several cleaners were tested and an alkaline cleaner called Fremont 776 was chosen as a replacement solvent. Aero Precision decided to convert the existing degreaser to an aqueous

TABLE 6.2 - NADEP COST BENEFIT ANALYSIS[40]

ANNUAL COSTS	SPRAY WASHER	VAPOR DEGREASER
Material Usage:		
Makeups (gal/yr)	100	16,000
Additions (oz/yr)	4800	0
Material Cost ($)	795.00	61,440.00
Steam Usage (lb/yr)	13,728	4,529,408
Energy Cost ($)	109.82	36,235.26
Water Usage (gal/yr)	0	570,000
Rinse Water Cost ($)	0.00	256.50
Production Labor (hr/yr)	1,040	2,080
Labor Cost ($)	16,848.00	33,696.00
Maintenance Labor (hr/yr)	50	100
Labor Cost ($)	1,220.00	2,440.00
Engineering Labor (hr/yr)	0	12
Labor Cost ($)	0.00	342.00
Rejected Parts (#/yr)	0	0
Rejection Cost ($)	0.00	0.00
Solid Waste (lb/yr)	3,500	48,000
Waste Disposal Cost ($)	1,750.00	58,800.00
TOTAL OVERALL COST ($)	20,722.82	193,209.76
TOTAL WASTE SAVINGS (lb/yr)	44,500	
TOTAL COST SAVINGS ($)	**172,486.94**	

system, which alleviated them from having to purchase a new unit. For a summary of their economic analysis, refer to Table 6.3.

6.5.3 Vandenberg Air Force Base[24]

TCA is typically used in degreasing operations at Vandenberg Air Force Base, CA. Due to increasing liabilities and disposal costs associated with this chlorinated solvent, a program was started to find an alternative cleaner. Two alternatives were examined for minimizing solvent waste and solvent emissions: substitution of TCA with an aqueous alkaline cleaner and the installation of a refrigerated freeboard chiller. The researchers at Vandenberg conducted tests and determined that the best alternative for solvent waste reduction was the incorporation of an aqueous alkaline cleaning system. The following key points summarize the justification for the researchers decision:

1. The annual cost for using TCA was $27,260/yr compared to the alkaline cleaner cost of $15,820/yr, reducing cost by 40 percent and saving $11,440/yr.

2. Hazardous waste generation was reduced by 70 percent by substituting TCA with an alkaline degreaser, decreasing disposal costs.

3. In addition to waste reduction, solvent emissions were eliminated since the alkaline cleaners is nonvolatile. This removes the threat of being exposed to toxic chemicals, giving workers a solvent-free environment.

TABLE 6.3 - AERO PRECISION ENGINEERING ECONOMIC EVALUATION[30]	
VAPOR DEGREASER COSTS:	**($/yr)**
Solvent (479 gallons/yr)	2,700
Solvent Disposal (150 gallons/yr)	150
Electricity	335
Maintenance	1,500
Water	50
TOTAL	4,735
ALKALINE CLEANER COSTS:	
Detergent (1200 gallons/yr)	850
Electricity	583
Maintenance	1050
Water (use under 1000 gallons/yr)	50
TOTAL	2,533
SAVINGS	2,202

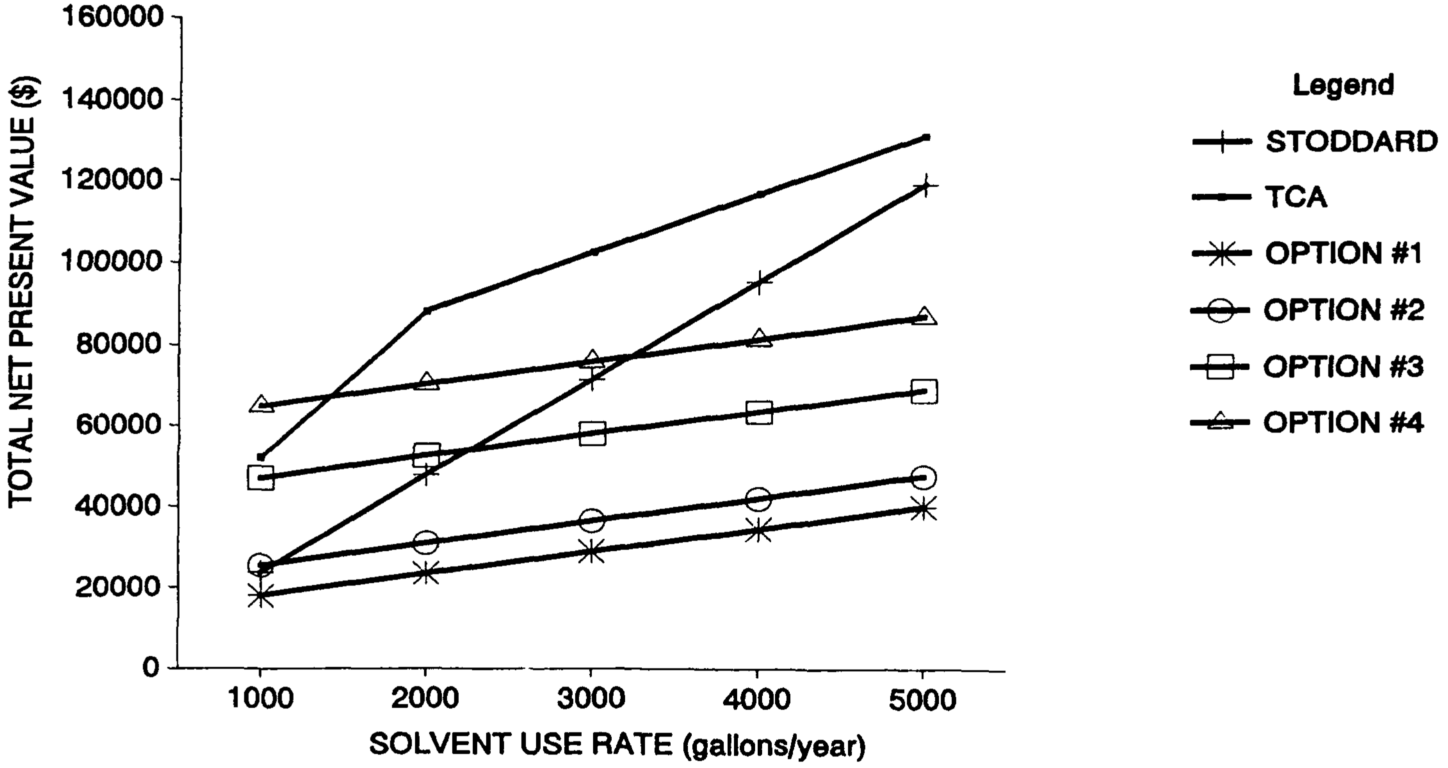


Figure 6.1. Alkaline Cleaner Comparison at 10:1 Dilution With Generation of Nonhazardous Waste.[1]

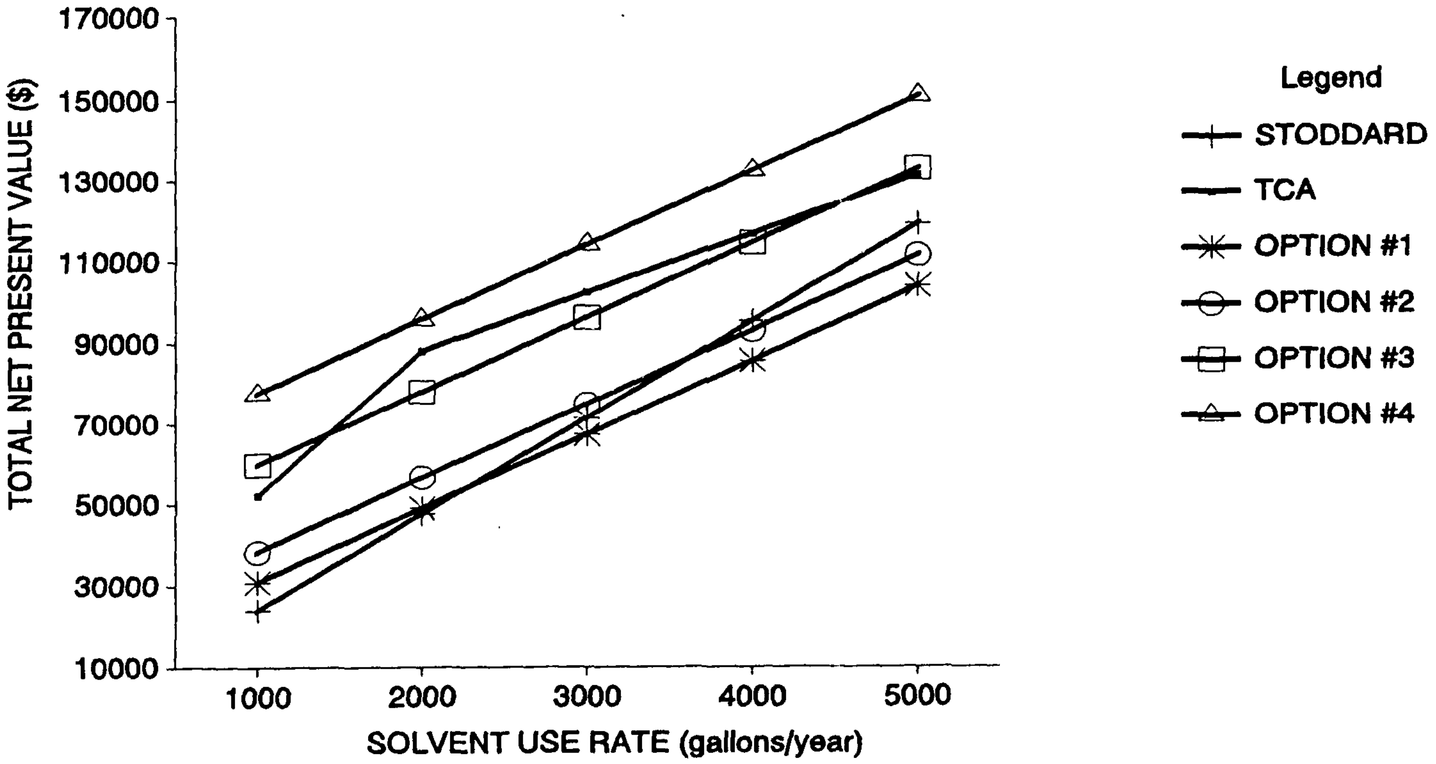


Figure 6.2. Alkaline Cleaner Comparison at 3:1 Dilution With Generation of Nonhazardous Waste.

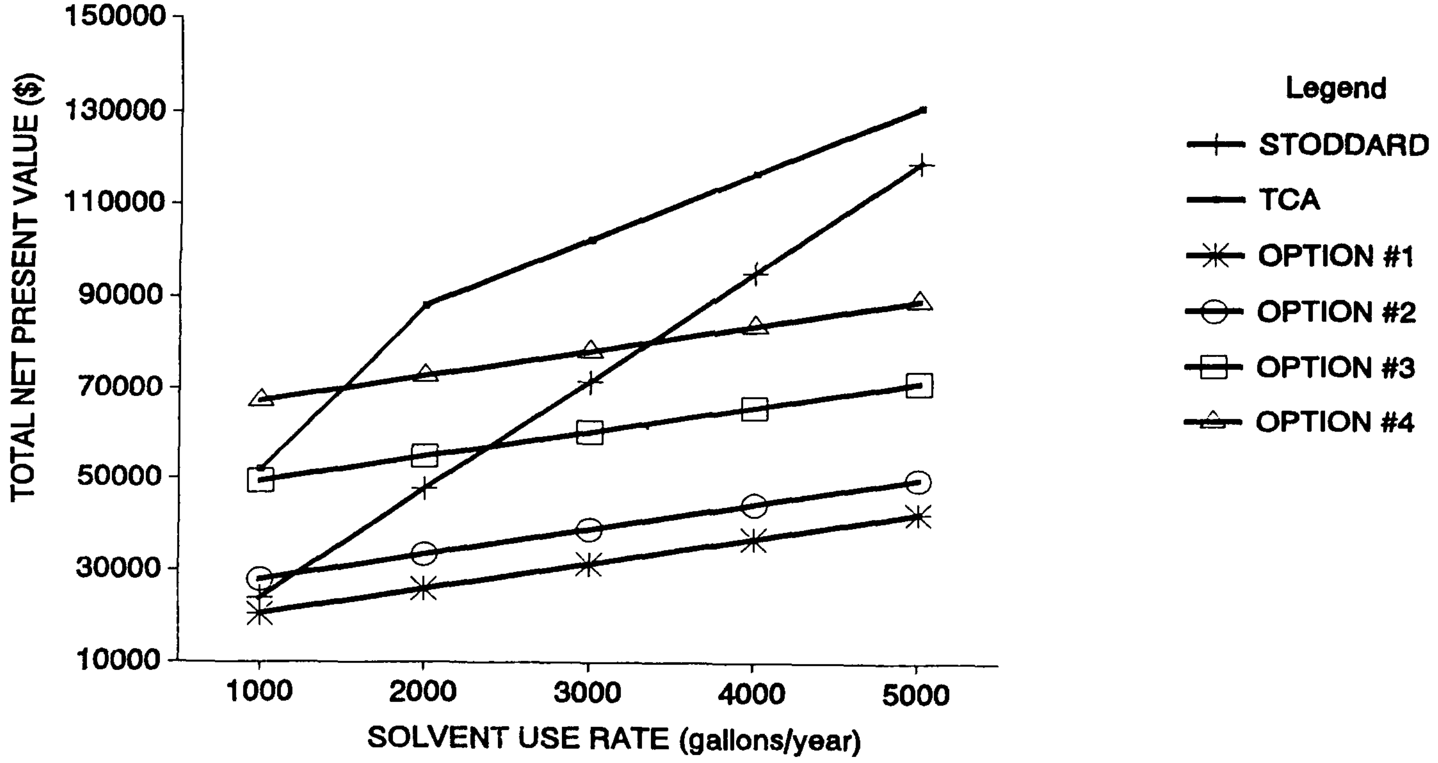


Figure 6.3. Alkaline Cleaner Comparison at 10:1 Dilution With Generation of Hazardous Waste.

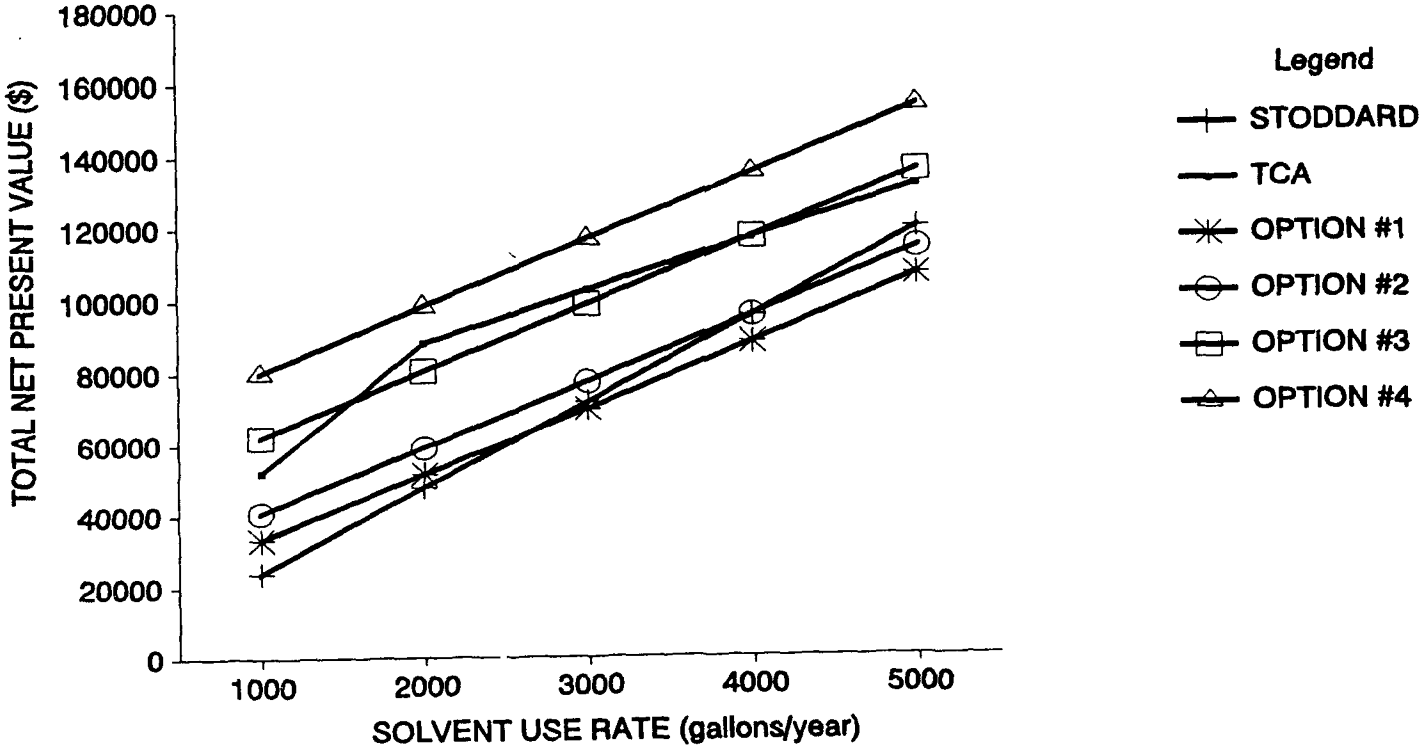


Figure 6.4. Alkaline Cleaner Comparison at 3:1 Dilution With Generation of Hazardous Waste.

Chapter 7

Synthesis and Discussion

7.1 Background

Are alkaline cleaners a feasible alternative for organic solvents in metal parts degreasing operations? This chapter analyzes this question by performing a comparison of the metal degreasers covered in the previous chapters. To accomplish this task, certain solvent properties will be discussed to determine the environmental and economic impacts of the material substitution. The solvent properties that will be examined in this chapter include:

1. Chemical and Physical Properties
2. Toxicity
3. Reactivity
4. Biodegradability
5. Cleaning Efficiency
6. Recycling
7. Disposal Methods
8. Economics.

Based on the literature searches, case studies, and economic evaluations, these sections will provide the insight necessary to determine if alkaline cleaners are an alternative for organic solvents at U.S. Army installations.

7.2 Chemical Properties

Stoddard solvent is a nonhalogenated cleaner composed of paraffinic, naphthenic, and aromatic hydrocarbons. As mentioned in the literature review, the proportions of these compounds present in the crude oil (before distillation) greatly affect the solvency power, as well as other properties of the solvent. For example, the aliphatic hydrocarbons present in the oil make the solvent only slightly soluble and can help reduce the boiling point.[25] Paraffins help dissolve the grease and determine the cleaning ability of the solvent on metal parts.

1,1,1-Trichloroethane (TCA) is a halogenated solvent produced by a chemical reaction of hydrogen chloride and 1,1-dichloroethylene in the presence of a ferric chloride catalyst. Another process used to manufacture TCA is by hydrochlorinating vinyl chloride to 1,1-dichloroethane, which can then be thermally or photochemically chlorinated to form TCA.[17] Due to the unstable nature of the solvent, a stabilizing agent must be introduced to prevent decomposition. Many stabilizing systems have been developed to protect the solvent from degrading due to exposure to metals, air, light, and temperature. Examples of stabilizing agents used include 1,4-dioxane, epoxide, alcohols, and nitro compounds.[26] TCA is especially sensitive to metals and must be specially stabilized to prevent decomposition of the vapor during degreasing operations.

Alkaline cleaners are typically composed of water and chemical additives, consisting of builders, surfactants, and complexing agents.

Builders are required for neutralization of acidic soils and assist in dispersion. Common builders found in alkaline cleaners include sodium and potassium hydroxide, silicates, phosphates, and carbonates.

Surfactants are typically synthetic detergents that provide the wetting and emulsifications properties needed for soil removal. The three major types of detergents manufactured are anionic (negative charge on surface active ion), non-ionic (neutral charge), and cationic (positive charge).

Complexing agents are used in alkaline cleaners to avoid precipitation and staining, metal activation, and water softening. Typical classes of complexing agents include alkanolamines, gluconates, polycarboxylic, acids, and phosphonates.

In some cases, commercial alkaline cleaners will contain a solvent (typically 9 to 10 percent by weight) to help in the emulsification process. Solvents found in cleaners today include diethylene gycol n-butyl ether, n-butoxyethanol, and dipropylene gycol methyl ether.

7.3 Physical Properties

• Stoddard Solvent

1. Stoddard solvent possesses a high boiling point that can cause problems during distillation. However, with the use of a vacuum, the boiling point of Stoddard solvent can be reduced to a temperature below its flash point, decreasing the risk of ignition.

2. The flash point of Stoddard solvent can vary depending on the type used (100 to 140 °F). Typically, Stoddard solvent with a 140 °F flash point is used at Army installations for safety reasons. However, even with the higher flash point, the solvent is a combustible material that can be easily ignited from a heat source. The vapors given off are also explosive and caution should be used to avoid accidental ignition.

3. The evaporation rate of Stoddard solvent is relatively small when compared to TCA. However, this solvent is still a volatile substance and tends to evaporate rapidly in open air. The advantage of this characteristic is that no additional equipment is necessary for drying upon completion of the cleaning cycle. The disadvantage of the solvent's high volatility is that extra ventilation may be required to avoid a build-up of harmful vapors. Air regulations may require the ventilated air be cleaned before releasing it into the atmosphere. This would add an extra cost for Stoddard solvent use.

4. Stoddard solvent possesses a kerosene-like odor. This odor can become annoying, and prolonged exposure to the solvent has caused nose and throat irritation.

• 1,1,1-Trichloroethane

1. TCA possesses a very low boiling point, approximately 165 °F at one atmosphere. The low boiling point allows for easy separation of the contaminants from the solvent with simple distillation. However, due to the low boiling point, special precautions need to be taken to ensure that the vapors do not escape into the environment. This increases operating costs.

2. TCA is a relatively nonflammable substance and exhibits no flash point according to standard laboratory tests. For this reason, TCA is an ideal choice for vapor degreasing operations that operate at elevated temperatures.

3. The evaporation rate for TCA is fast (approximately five times greater than Stoddard solvent) due to the solvents high vapor pressure. In cleaning operations, this allows for rapid drying of parts without the use of drying equipment, which is similar to Stoddard solvent. Due to TCA's involvement in ozone depletion, strict emission regulations must be followed to prevent the solvent vapors from escaping into the air. Most modern facilities have adsorption mechanisms, low temperature traps, and lock systems to handle the harmful vapors, which enables the cleaning operation to function safely.

4. TCA exhibits a low solubility in water. Based on the solubility, the organic carbon partitioning coefficient (K_{oc}) for this solvent is 155.[14] This gives the solvent moderate mobility due to its tendency to be adsorbed by soils. Because of this physical property, water collected from vapor degreasers must be treated before being released into the environment to prevent soil contamination.

- **Alkaline Cleaners**

1. The boiling point of most alkaline cleaners is around 212 °F, which is the boiling point of water. The high boiling point allows the cleaner to operate at elevated temperatures for more efficient soil removal. This characteristic makes the alkaline cleaner an ideal candidate for a replacement solvent in vapor degreasing operations. With some minor modifications, existing tanks can be converted at low cost.

2. Alkaline cleaners are nonflammable and exhibit no flash point. This is primarily due to the cleaner being mostly water. This physical property eliminates the need for special handling and storage procedures and decreases the probability of accidental fires or explosions in the work place.

3. Typically, alkaline cleaners are nonvolatile and possess an evaporation rate comparable to water. Extra ventilation is not required with this process and replacement costs, associated with organic solvent losses during vapor degreasing operations, are eliminated. Generally, in alkaline cleaning systems, only water must be replaced periodically to maintain the proper operating conditions in the tank. A disadvantage of its slow evaporation rate is the drying time. Depending on the operation, drying equipment may be needed to achieve the necessary cleaning efficiency.

4. Alkaline cleaners are completely water soluble and can either emulsify oils or cause water to penetrate and lift the oil from the part, allowing the oil to float on the surface (the cleaner formulation will dictate which reaction occurs). Cleaners that emulsify oils must be neutralized and the oiled removed before being discharged into a sewer system. This is usually accomplished with an additive, typically acetic acid, which lowers the pH causing the oils to recoagulate and float to the surface. Once this is done, the oils can be removed and the cleaner discharged without any adverse effects on the environment.

5. Alkaline cleaners generally operate at high pH levels (11-13). Therefore, excessive contact without protective equipment (e.g., gloves, goggles) should be avoided to prevent any unnecessary irritation. Before the cleaner is incorporated into the cleaning process, tests should be done to ensure the high pH does not adversely affect the metal being degreased. For example, aluminum is sensitive to high pHs, which can cause the surface to be etched. To compensate for this problem, some alkaline cleaners contain sodium metasilicate. This chemical causes a reaction that forms a thin film over the metal, protecting it from corrosion.

7.4 Toxicity

Stoddard solvent has been recognized as a hazard due to the acute and chronic effects it has on workers exposed to it. Epidemiological studies have documented these effects, which consist of fatigue, irritability, memory loss, mood changes, and impaired intellectual function. Because of Stoddard solvent's toxicity concerns it has been assigned a low threshold limit value (TLV) of 100 ppm. This value was based on toxicity analyses performed on Stoddard solvent's major components to determine a limit that would prevent the acute and chronic effects from occurring.[28] Toxicity studies performed on animals have also shown that exposure to Stoddard solvent could result in physiological damage. Rats exposed to the solvent at 300 ppm, for 5 days/week for 13 weeks, have shown signs of kidney damage. An 8-hour exposure at 290 ppm produced minor congestion and emphysema in guinea pig lungs.[25] Fifty percent of the test population died (LD_{50}) at dosage levels from 5660 mg/kg (rabbits) to 9470 mg/kg (guinea pig).[22]

Stoddard solvent enters the body through inhalation, ingestion, and skin and eye contact. Inhalation of this substance can lead to irritation of the lungs, resulting in edema.[25] Ingestion can cause death; therefore, immediate medical attention is required. Contact with this solvent can lead to dryness and irritation due to the defatting action on the skin. Contact with the eyes should especially be avoided to prevent any optical damage.

TCA has been categorized as moderately toxic with effects ranging from mild irritation to death. At low concentrations (500 ppm), mild irritation on the skin and mucosa have been recorded along with decreases in the psychomotor skills. At high concentrations (2600 ppm), human test subjects exhibited narcotic effects and were unable to stand unsupported.[26] Deaths that occurred from high levels of exposure to TCA resulted from respiratory paralysis and, in some cases, from cardiac arrest. Animals exposed to low concentrations of solvent showed similar acute symptoms of skin and mucous membrane irritation. After long periods of inhalation, some animal specimens developed chromosomal damage in the brain. The LD_{50} for rats and mice subjected to TCA was 11 g/kg body weight.[26]

Routes of entry for TCA include inhalation, skin adsorption, eyes, and ingestion. Eye irritation is usually noted first when a person has contact with the solvent. Mild conjunctivitis (irritation of the mucous membrane lining of the eyelid) may develop from exposure to the vapor, but recovery is usually rapid.[28] TCA also possesses defatting properties, and if contacted with the skin it can produce dermatitis. As mentioned in the above paragraph, inhalation of the solvent can cause dizziness, incoordination, unconsciousness, and death. If TCA is ingested, induced vomiting and immediate medical assistance is recommended.

Due to the wide variety of alkaline cleaners on the market, numerous material safety data sheets were compared to determine some common links on the toxicity of alkaline cleaners. Based on the information gathered, none of the cleaners contained carcinogenic ingredients or possessed any carcinogenic characteristics. Alkaline cleaners were observed to be relatively innocuous and nontoxic. Acute and chronic disorders consisted mainly of skin and eye irritation, which can be controlled with the use of proper protective equipment. However, as mentioned in the previous text, some cleaners contain a small amount of solvent (approximately 9 percent by weight in concentrated form) used in oil emulsification. In concentrated form the solvent present in the alkaline cleaner could cause some toxicity concerns, but under normal operating conditions the solvent is diluted in the bath solution to low concentrations (less than 0.01 percent). The case study conducted by the Idaho National Engineering Laboratory, under direction of the Air Force, eliminated an alkaline cleaner from further testing because it contained 2-butoxyethanol. The report explains that even though exposure levels to the solvent would not be exceeded (under normal operation conditions), the Air Force was concerned that future restrictions might eliminate its use. Another commercial alkaline cleaner, Blue Gold, was tested by an independent laboratory to determine toxicity. Test results showed that the rats, rabbits, and mice exposed to the cleaner did not manifest any toxic effects.

Routes of entry for alkaline cleaners generally was through ingestion and contact with the skin and eyes. If cleaner is splashed in the eyes, a mild irritation will occur. Flushing with water should alleviate the problem without any lasting effects. Prolonged contact with alkaline cleaners may cause dry skin or irritation due to the natural oils being removed from the skin surface. If ingested, water should be administered to dilute the cleaner followed by a mild acidic substance to neutralize the alkalinity.[3,18] Death will not result from ingestion; however, diarrhea can occur.

7.5 Reactivity

Stoddard solvent has been observed to be a fairly stable substance (under normal conditions) during storage and handling. Due to the solvent's low flash point, all ignition sources should be avoided to prevent a fire. Stoddard solvent is reactive with strong acids and bases, oxidizing agents, and selected amines.

TCA is a moderately reactive substance that is incompatible with strong caustics, strong oxidizers, and chemically active metals. The solvent's chemical characteristics make it highly unstable, causing rapid decomposition when exposed to the open air. In the atmosphere, TCA reacts with hydroxyl radicals, ozone, and other atmospheric substances, which helps in the catalytic degradation of the ozone layer. For this reason, legislation has been initiated to eliminate TCA.

Alkaline cleaners are not reactive and are stable under normal conditions for storage and handling. Presently, no materials have been found that are incompatible with alkaline cleaners and no hazardous decomposition has been exhibited with this product. As a result, no special facilities or precautions need to be established for warehousing the product, decreasing the Army's liability.

7.6 Biodegradability

This section focuses mainly on the biodegradation of alkaline cleaners, since Stoddard solvent and TCA are not biodegradable. A detailed study was conducted at Tinker Air Force Base by the Idaho National Engineering Laboratory to find a suitable biodegradable solvent to replace the hazardous solvents currently being used. This study, mentioned in Chapter 5, examined many solvents based on their solubility, cleaning efficiency, corrosiveness, and biodegradability. Preliminary testing narrowed the field to four cleaners, two of which were alkaline. Extended tests were then performed on the remaining four solvents to ensure they meet the proper specifications. To determine if these solvents were biodegradable, biological acclimation tests were performed to examine the effect of the cleaners on a waste water treatment facility. The biological analysis was divided into two phases. The first phase was to perform a series of 8-day acclimation tests to see if the microorganisms would adjust and degrade the solvent. The second phase involved a pilot study at a waste water treatment plant to observe the effects the cleaner has on the system. The following paragraphs discuss the results of the study on the biological acclimation of the two alkaline cleaners tested.

The first alkaline cleaner tested is known commercially as 3D Supreme and is a typical example of a mild alkaline degreaser available today. During the 8-day acclimation tests, the organisms were able to degrade the solvent adequately. This was evident by the reduction in the Chemical Oxygen Demand (COD) and the Total Organic Carbon (TOC). However, during the pilot plant study, 3D Supreme did not biodegrade. A gas chromatography analysis clearly showed the presence of solvent in the effluent from the final clarifier. The COD concentrations showed no significant increases or decreases in the system (see Figure 7.1). The TOC concentrations fluctuated widely, but some reductions were observed between

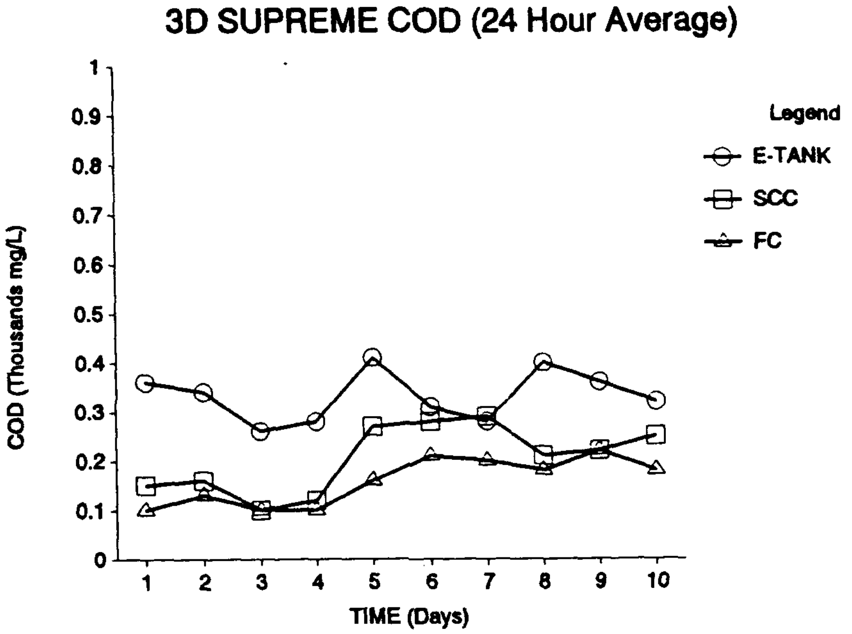


Figure 7.1 - COD Concentrations During 3D Supreme Pilot Plant Study (24 Hour Averages).[21]

the equalization tank (E-tank), solid contact clarifier (SCC), and final clarifier (FC) (see Figure 7.2). The main reason the solvent did not degrade was due primarily to the presence of phenol in the waste stream. The microorganisms in the activated-sludge were selectively feeding on the phenol and ignoring the solvent as a food supply. As a result, as long as phenol was present in the waste stream, the organisms would not adjust and degrade the alkaline cleaner. The report states the solution to this problem would be to remove the phenol from the waste stream and provide a continuous feed of solvent to the system, giving the organisms a chance to acclimate. Also, neutralization of the solvent before entering the wastewater stream would make handling the solvent more convenient and cost effective.

Another problem that occurred during biodegradation was flotation of the sludge due to the presence of the cleaner. To prevent this from happening, small amounts of ferric chloride were added to the treatment plant process stream. The expenses for the chemicals and equipment were estimated to be costly. The addition of 50 mg/L of ferric chloride would cost $391 per million gallons of water treated for the chemicals alone.[21] The use of an iron bearing polymer could help reduce the costs; however, this was not verified in the report. 3D Supreme did not adversely affect the organisms in the sludge during the testing. This was evident from the nitrogen, ammonia, and phosphorous concentrations remaining constant during the testing. Any increase in concentration would indicate a problem with the system. Also, chromium and zinc levels were unaffected by the addition of the ferric chloride; however, the iron did increase in the effluent.

Fremont 776 was the next alkaline cleaner tested at the waste water treatment plant. This cleaner had a different chemical formulation than 3D Supreme. It was composed mostly of sodium metasilicate and did not contain any organic constituents. Fremont 776 was substituted during later stages of the study to replace another cleaner eliminated due to toxicity concerns. The Air Force requested this cleaner because it was already being used in spray washers for cleaning fuel assemblies. Due to the solvent being a late entry, the 8-day acclimation test was not performed. Only the pilot plant analysis was conducted

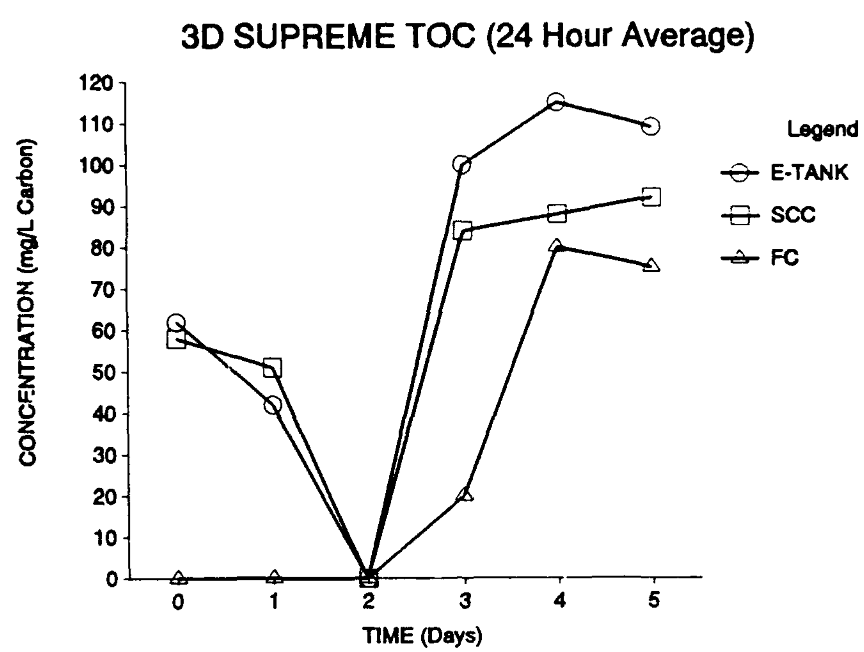


Figure 7.2 - TOD Concentrations During 3D Supreme Pilot Plant Study (24 Hour Averages).[21]

for this cleaner. The results of the study indicated that, due to the solvent being composed of mostly sodium metasilicate, which is inorganic, the organisms were unable to degrade it. However, this was not a concern because sodium metasilicate has no impact on the National Pollution Discharge Elimination Standards (NPDES) regulations and does not have to be degraded. Fremont 776 did not cause the sludge to float and requires no addition of ferric chloride. But after the solvent was added to the wastewater stream, the effluent became turbid, and it took the SCC several days to filter out the particles that caused the problem. Ammonia, nitrogen, and phosphorous concentrations did not increase during testing, indicating no adverse effects on the microorganisms due to solvent exposure. COD concentrations remained constant and were unaffected by the addition of the cleaner. The TOC concentrations fluctuated, but a consistent drop could be observed between the E-tank, SCC, and FC (refer to Figures 7.3 and 7.4). Increases in chromium and iron were detected; however, this was due to the change in the influent stream and not a result of the cleaner. Zinc concentrations remained constant during the testing.

It can be concluded from the data that each alkaline cleaner affects the treatment process differently. But as indicated in the study, modifications to the process can be incorporated to make the system functional. This study helps emphasize the importance of preliminary testing, which is needed to design and implement an alternative alkaline cleaning system.

7.7 Cleaning Efficiency

Stoddard solvent and TCA have been used, for many years, as degreasing solvents in metal parts cleaning. These solvents have proven to yield high cleaning efficiencies and protect bare metal surfaces from corrosion during the cleaning process.

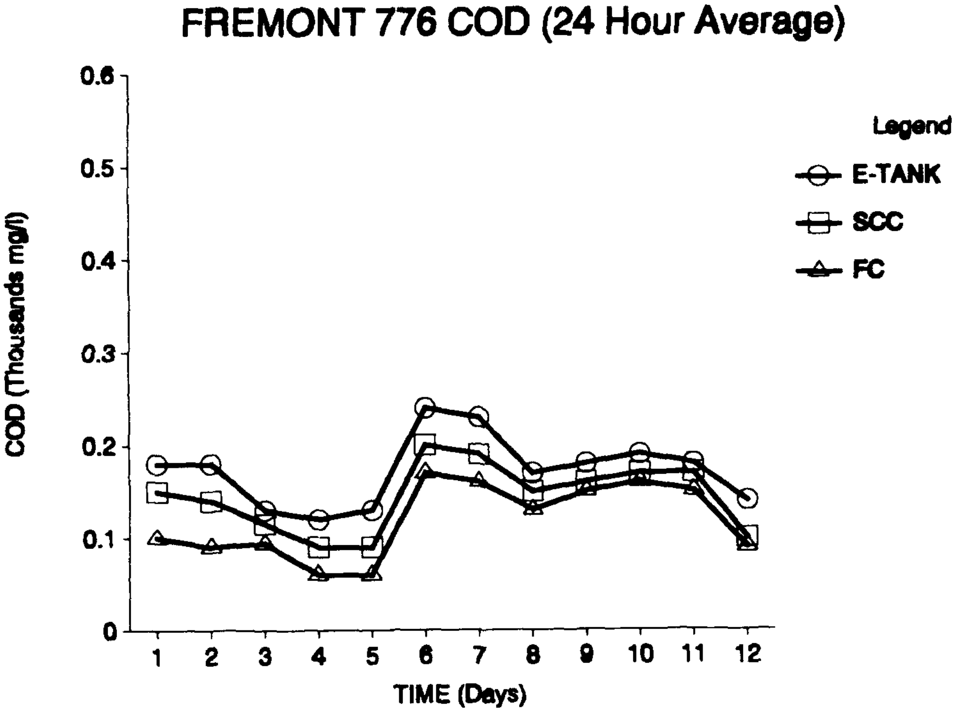


Figure 7.3 - TOC Concentrations During Fremont 776 Pilot Plant Study (24 Hour Average).

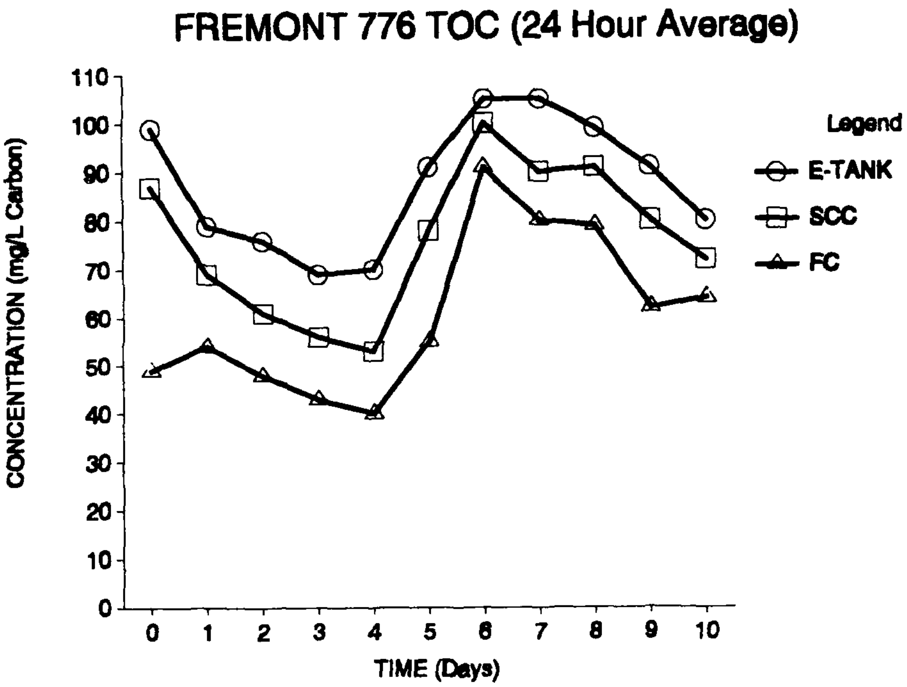


Figure 7.4 - TOC Concentrations During Fremont 776 Pilot Plant Study (24 Hour Average).[21]

To compete with organic solvents, alkaline cleaners must posses comparable cleaning efficiencies without promoting corrosion. Numerous research facilities have conducted investigations on the cleaning ability of alkaline cleaners. The studies examined cleaning times, corrositivity, and cleaning enhancements to determine the cleaning efficiencies of these water-based detergents. The following paragraphs discuss the results of these studies to show the potential of alkaline cleaners as a replacement solvent.

The research facility at the Paducah Gaseous Diffusion Plant was involved in cleanliness and corrosion testing on a number of alternative solvents. One of the first goals of this project was to devise a method to measure the cleaning ability of the solvents tested. It was determined that measurements of the surface energy, before and after cleaning, would provide the information needed to define the cleanliness of the metal. The procedure for this analysis involved preparing 11 solutions with varying specific gravities ranging from 0.85 to 1.53. Each solution was then numbered from 1 to 11 in order of increasing surface tension. The cleaned test specimen was then immersed in the solution and observations noted. A clean surface would have a high surface energy and tend to spread out when dipped into the solution. Conversely, a dirty surface would have a low surface energy causing the liquid to bead. Based on this procedure the cleanest surface is one that has a surface energy greater than solution 11. Blue Gold was the only alkaline cleaner tested in this study. This cleaner was tested in an immersion tank and an ultrasonic tank. In the immersion tank the dilution and temperature during testing was 20:1 and 145 °F. In the ultrasonic tank the concentration and temperature was 20:1 and 76 °F. The cleaning times are shown in Table 7.1 and are based on specimens with cleanliness ratings greater than 11. Other observations during testing were that Blue Gold rinsed freely from metal surfaces, and no breakdown products were found in the spent solution.

Corrosion tests were also performed at Paducah to determine the corrosion rates and pitting tendencies of the cleaners on certain metals. The results from the analysis found that the alkaline cleaner Blue Gold had the lowest corrosion rate of all the cleaners tested (see Table 7.2). Other data from the investigation revealed that pitting is possible; however, the time to initiate the pitting is typically longer than the contact time in a degreasing operation.

The study performed at Tinker Air Force Base also conducted extensive cleaning efficiency tests on alkaline cleaners. The main objective of the analysis was to test the cleaner's ability to remove soils commonly found on aircraft parts, including hydraulic fluid, molybdenum disulfide grease, and a carbonized oil/xylene mixture. Cleanliness of the parts was to be determined by the "white glove test," which means, if a residue can be wiped from the part, it is not considered clean. Additionally, a fluorescent penetrant oil was used to help in cleanliness testing. Residue from a cleaner tends to interfere with the fluorescent oil, simplifying the detection of flaws. Three cleaning processes were tested in this study: immersion with no agitation, immersion with agitation, and ultrasonics. The ultrasonic unit was tested at three different settings: 300, 600, and 900 watts.

Ultrasonics at the 900 watt setting tended to increase the temperature of the water above normal operating ranges. Therefore, it was decided that all ultrasonic tests be operated to maintain a water temperature below 140 °F to ensure maximum cleaner performance. Two cleaners, 3D Supreme and Fremont 776, were the only alkaline products tested at Tinker Air Force Base. However, due to the late entry of Fremont 776, 3D Supreme was the only cleaner tested during this phase of the project. Results of the cleaner's performance are shown in Table 7.3. Rinsing tests performed on 3D Supreme were satisfactory. A 99.9 percent removal efficiency was achieved after cleaning the hydraulic fluid, and an 82 percent removal efficiency was achieved after cleaning the molybdenum disulfide grease. 3D Supreme also passed drying tests with 93 percent of the solvent being evaporated in 5 minutes and 99 percent of the solvent being evaporated in 20 minutes.

TABLE 7.1 - SUMMARY OF CLEANING TIMES FOR PADUCAH GASEOUS DIFFUSION PLANT STUDY[15]

SOILS	BLUE GOLD IMMERSION (seconds)	BLUE GOLD ULTRASONIC (seconds)	TCA (seconds)
FINGERPRINTS/DUST			
MONEL	15	15	90
STEEL	15	15	60
COPPER	30	15	90
ALUMINUM	15	15	20
PHOSPHOR BRONZE	15	15	150
LUBE OIL			
MONEL	30	30	460
STEEL	30	30	1200
COPPER	120	60	900
ALUMINUM	30	30	1200
PHOSPHOR BRONZE	60	60	420
WATER-SOLUBLE OIL			
MONEL	15	15	120
STEEL	15	15	120
COPPER	15	15	120
ALUMINUM	15	15	120
PHOSPHOR BRONZE	15	15	120
PETROLEUM GREASE			
MONEL	16,200	540	21,600
STEEL	16,200	540	21,600
COPPER	16,200	540	21,600
ALUMINUM	16,200	540	21,600
PHOSPHOR BRONZE	8,100	60	21,600
SILICONE GREASE			
MONEL	9,000	1,320	21,600
STEEL	9,000	1,320	21,600
COPPER	9,000	1,920	21,600
ALUMINUM	9,000	960	21,600
PHOSPHOR BRONZE	9,000	1,440	21,600

During Phase III testing at Tinker Air Force Base, additional cleaning efficiency analyses were performed, including a 100 gallon test, cabinet spray washer test, and a full-scale analysis. Both alkaline cleaners, 3D Supreme and Fremont 776, were involved during this phase of the study.

The 100-gallon test was designed to see how the solvents would perform at a larger scale. The system was equipped with a turbo washer designed to create vigorous agitation within the tank. Both cleaners performed satisfactorily, removing 94 percent of the oil and grease from aircraft components within 30 minutes. The water-based solvents also removed a higher percentage of carbon from the parts than did the organic-based solvents (refer to Figures 7.5 and 7.6).

TABLE 7.2 - PADUCAH GASEOUS DIFFUSION PLANT CLEANER CORROSION RATES (mils per year)[15]

METALS	CLEANERS	CORROSION RATE at 77°F	CORROSION RATE at 140°F
Monel	Blue Gold	0.05	0.11
	Tivaclean	0.08	0.15
	Chem-Crest	0.07	0.11
Steel	Blue Gold	0.08	0.17
	Tivaclean	0.08	0.35
	Chem-Crest	0.07	0.18
Copper	Blue Gold	0.38	1.31
	Tivaclean	0.48	4.64
	Chem-Crest	1.60	3.91
Aluminum	Blue Gold	0.10	0.16
	Tivaclean	0.25	1.15
	Chem-Crest	0.18	0.25
Phosphor Bronze	Blue Gold	0.21	1.19
	Tivaclean	0.50	4.35
	Chem-Crest	1.74	5.61

The cabinet spray washer experiment tested how 3D Supreme would clean when used in this type of system. Since Fremont 776 was already being used by the Air Force in spray washing, testing was not necessary. Results of the testing showed that at a 20:1 dilution, 3D Supreme effectively removed all the oil and grease within 10 minutes. Carbon removal proved more difficult, but after 30 minutes only light deposits were observed on the parts. During the full-scale testing, a 300-gallon tank was equipped with a 7.5 horsepower electric pump, which created intense agitation. Both alkaline cleaners achieved excellent cleaning efficiencies during this analysis. Within a 15-minute cleaning period, 100 percent of the oil and grease plus a high percentage of carbon had been removed from the parts (refer to Figure 7.7). The increased performance in the full-scale test, compared to the 100 gallon test, was primarily due to more intense agitation achieved by the use of a larger pump.

Corrosion of metals during cleaning was also researched at Tinker Air Force Base. Extended testing was performed on different metals to observe their reaction when exposed to 3D Supreme and Fremont 776 (refer to Table 7.4). Based on the results, using a 0.3 mils/year limit, 3D Supreme exhibited light corrosion on most of the metals tested, with excessive corrosion noted on aluminum and magnesium. Fremont 776 was more effective in preventing corrosion, maintaining the project's 0.3 mil/year limit.

General Dynamics performed a study on a number of alkaline cleaners for use as alternative solvents in their vapor degreasing operations. Out of the 46 cleaners tested, four water-based alkaline detergents were chosen as possible candidates for substitution. Table 7.5 lists cleaning efficiency results for the cleaners. Experiments were conducted in a 3-gallon aluminum tank, with mild agitation to simulate normal operating conditions.

7.8 Recycling

The recovery of Stoddard solvent and TCA has proven to be an efficient process and is commonly used at many U.S. Army installations. Two recycling methods practiced are onsite distillation and contract/leased recycling. Onsite recycling is typically accomplished by the use of distillation stills, which

TABLE 7.3 - CLEANING EFFICIENCIES FOR 3D SUPREME											
SOILS	PROCESS ENHANCEMENTS										
	No Agitation		Mixer Agitation at 500 rpm			Mixer Agitation at 650 rpm				Ultrasonic at 300 watts	
Hydraulic Fluid	120°F	140°F	100°F	120°F	140°F	77°F		100°F		77°F	
	95%	97%	98%	99%	99%	95%		97%		100%	
Molybdenum Disulfide Grease	140°F		100°F	120°F	140°F	77°F	100°F	120°F	140°F	77°F	100°F
	99%		92%	97%	100%	58%	95%	95%	100%	99%	100%

* These results are for a 10 minute cleaning period.

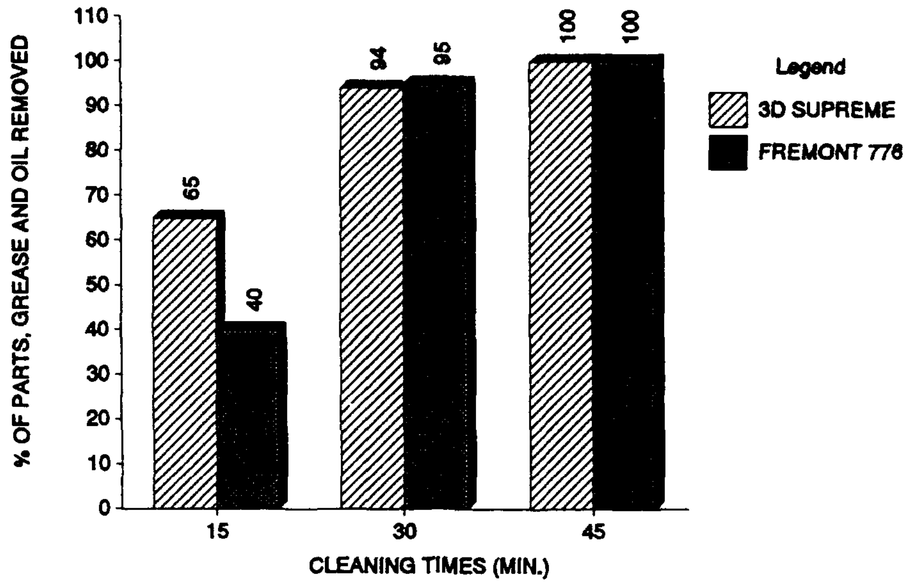


Figure 7.5 - Oil and Grease Removal During the 100-Gallon Test.[21]

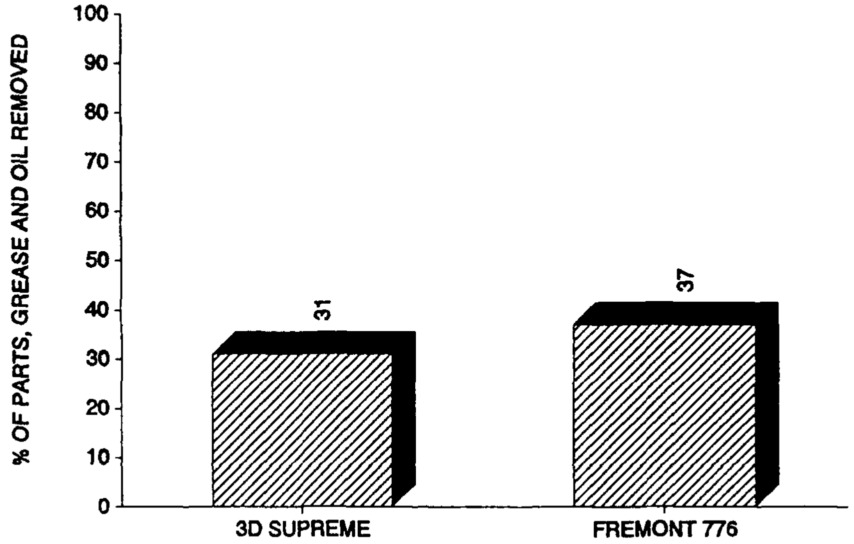


Figure 7.6 - Carbon Removal During the 100-Gallon Test.[21]

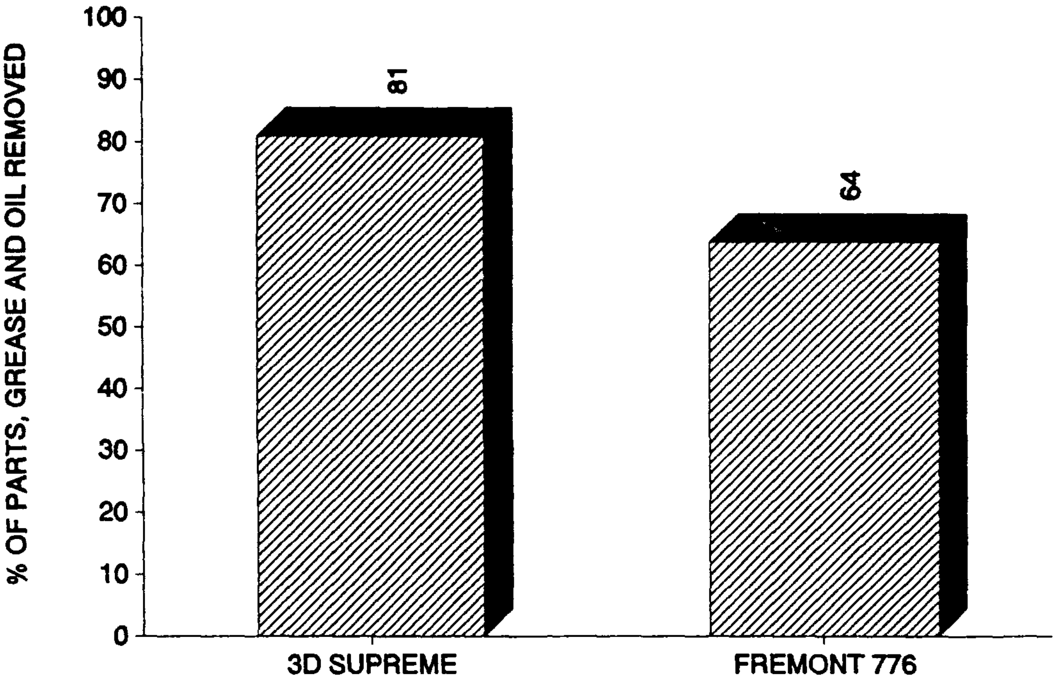


Figure 7.7 Carbon Removal During the Full-Scale Test.[21]

are able to separate the impurities from the contaminated solvents. The solvency power of the reclaimed solvent is unaffected; however, the inhibitors present in the solvent are lost during the distillation process. The distillation process residue must be collected and treated as hazardous waste. Offsite recycling, on the other hand, transfers the responsibility for reclamation to an outside contractor, relieving base personnel of handling and disposal.

Because of the biodegradable nature of alkaline cleaners, reclamation is not commonly practiced as part of the cleaning process. Typically, once the solution is contaminated, the bath is neutralized and dumped, and a new batch of cleaning solution is prepared. Ultrafiltration of alkaline cleaners was recently

TABLE 7.4 - TINKER AIR FORCE BASE CLEANER CORROSION RATES (mils per year)[21]

Metals	3D Supreme	Fremont 776
Copper	.35	0
Nickel	.47	.03
Aluminum	61.8	.11
Stainless Steel	.37	0
Monel	.22	.02
Waspaloy Alloy	.04	.01
Magnesium	727	0

*3D Supreme was at a 3:1 dilution @ 77 °F
*Fremont 776 was at a concentration of 6 ounces per gallon @140 °F

TABLE 7.5 - CLEANING TIMES FOR ALKALINE CLEANERS TESTED IN GENERAL DYNAMICS STUDY[39]

CONTAMINANTS	TURCO	BRULIN	QUAKER	DARACLEAN
TITEN LUBE	5 min. @ 140°F	10 min. @ 150°F	10 min. @ 130°F	5 min. @ 120°F
COSMOLENE	ineffective	ineffective	ineffective	ineffective
EP-2	5 min. @ 120°F	5 min. @ 140°F	5 min. @ 120°F	5 min. @ 140°F
CASTOR	5 min. @ 130°F	5 min. @ 150°F	5 min. @ 150°F	5 min. @ 120°F
HONEY OIL	5 min. @ 130°F	5 min. @ 150°F	10 min. @ 160°F	5 min. @ 120°F
PETROLATUM	5 min. @ 130°F	5 min. @ 140°F	10 min. @ 140°F	5 min. @ 130°F
BEES WAX	5 min. @ 130°F	5 min. @ 150°F	5 min. @ 140°F	5 min. @ 130°F
CARBOWAX	5 min. @ 130°F	5 min. @ 120°F	5 min. @ 120°F	5 min. @ 140°F
MILL MARKS	5 min. @ 120°F	5 min. @ 120°F	5 min. @ 120°F	5 min. @ 120°F
SHOP DIRT	5 min. @ 120°F	5 min. @ 120°F	5 min. @ 120°F	5 min. @ 120°F
JOHNSON WAX	5 min. @ 120°F	5 min. @ 120°F	5 min. @ 120°F	5 min. @ 120°F

investigated by General Dynamics as a possible recycling method. During one study that examined the use of alkaline cleaners as an alternative solvent for vapor degreasing, General Dynamics performed an ultrafiltration pilot test to determine the viability of this process for recycling. Three types of commercial alkaline cleaners were tested. Each cleaner was fed through the filter at a constant rate and concentration to identify membrane fouling characteristics. Ranges for the rates varied from 1 to 5 percent, and for concentrations, from 1 to 30 percent. Results of the tests showed that in most cases soil concentrations in the permeate were low (ranging from 0.001 to 0.25 percent) and approximately 93 percent of the alkaline salts were able to be recovered. The recovery of the surfactant constituents tended to be the limiting factor in the ultrafiltration analysis. Only one out of the three cleaners was able to maintain its surfactant constituents during filtration. Cleaning efficiencies before and after ultrafiltration are listed in Table 7.6.

The use of ultrafiltration as a recycling method can lead to large savings in cleaner cost. Regeneration through ultrafiltration can greatly extend the life of an alkaline cleaning bath, thereby decreasing the frequency of replacement and raw material cost. Additionally, the membrane filter elements are regenerable and can be used indefinitely. However, as seen in the General Dynamics study, not every cleaner is compatible with a filter membrane. It is therefore recommended that proper testing be performed on the selected cleaner with the filter membrane before incorporating the ultrafiltration system into the cleaning process.

7.9 Disposal

As discussed in the previous section, TCA and Stoddard solvent are generally recyclable, except for the residues generated during the distillation process. These residual byproducts are treated as hazardous and must be disposed of in accordance with local, state, and Federal regulations. Options for the disposal of Stoddard solvent, discussed in Chapter 3, include incineration, fuel substitution, surface disposal, and sale. Options for the disposal of TCA are not as flexible, consisting of only incineration or surface disposal in a hazardous landfill facility.

TABLE 7.6 - CLEANING RATES BEFORE AND AFTER ULTRAFILTRATION[39]

SOILS	TURCO 4215		BRULIN 815GD		QUAKER 624GD	
	BEFORE	AFTER	BEFORE	AFTER	BEFORE	AFTER
Houghton 431	1:00	2:00	:45	:45	1:00	1:00
Bees Wax	1:30	9:00	:45	1:00	1:30	3:00
Petrolatum	:15	:30	:15	:30	:15	:15
Cimflo	:15	:30	:15	:15	:15	:15
Castor Oil	:45	:45	:30	:30	:30	:30
EP-2	3:30	>15:00	4:30	5:00	3:00	10:00
PF-400	2:00	4:00	1:00	2:00	3:00	3:00
K34/36	:15	:15	:15	:15	:15	:15
H-11	:15	:30	:15	:15	:15	:30

* Data expressed in minutes:seconds.

Manufacturers claim that alkaline cleaners are biodegradable and can be disposed of in storm sewers or receiving waters after the solution has been neutralized and the contaminants such as oil and grease removed at a wastewater treatment facility. But this is not always the case, as witnessed in the pilot plant study performed at Tinker Air Force Base. Under full-scale operating conditions, one of the alkaline cleaners tested (3D Supreme) was unable to degrade and caused the activated-sludge to float. However, this occurrence was not due to the solvent being nonbiodegradable, it was due to the site-specific operating conditions present at the plant during testing. The study indicated that if proper procedures are used to regulate the influent concentration to the treatment plant the cleaner would be able to degrade, making disposal via sewer and treatment plant possible. This example illustrates the importance of preliminary testing before incorporating a cleaner into a treatment system. With the help of preliminary test data, difficulties can be diagnosed early and solutions devised to avoid disposal problems.

Oil, grease, and other contaminants must be removed before disposal at a wastewater treatment facility. Typically the cleaning solution pH is lowered and allowed to sit overnight. This forces the oils to coagulate and float to the surface. The contaminants can then be removed easily with an oil/water separator unit and containerized for further treatment.

7.10 Economics

In Chapter 6, a cost-benefit analysis was performed using the CEAMHW Economic Model to determine the feasibility of incorporating an alkaline cleaning system. Four alkaline cleaning options were examined and compared to organic solvents currently being used in degreasing operations at U.S. Army installations. The overall result of the analysis found that in most cases alkaline cleaners were feasible and could help reduce cleaning cost. For a more detailed discussion on model results, refer to Section 6.4.

7.11 Alkaline Cleaners vs. Terpene Cleaners

In Chapter 2, a previous study was cited that examined the use of terpene-base semi-aqueous cleaners as a replacement for Stoddard solvent. This section of the discussion compares the conclusions found in both the alkaline cleaner study and the terpene cleaner study and points out the differences and similarities between both cleaners.

Biodegradability
Both cleaners were presented as being biodegradable by the manufacturer. However, during full-scale operation, the ability of both cleaners to biodegrade was dependent on the site-specific operating conditions existing at the wastewater treatment plant. Because each installation has its own performance criteria for disposal of materials, a thorough site evaluation is recommended.

Flash Point
There was a large difference in this category. Concentrated terpene cleaners exhibit a flash point that varies around 120 °F. Because terpene cleaners containing d-limonene have a low flash point, they cannot be safely heated. This diminishes their use in vapor degreasers. Alkaline cleaners possess no flash point and can be heated. This property makes alkaline cleaners an ideal candidate for use in heated emersion degreasing operations.

Toxicity
Alkaline cleaners were found to be nontoxic and to contain no carcinogenic ingredients. Terpene cleaners contain d-limonene which has been shown to be a carcinogen that primarily attacks the kidneys, forming lesions. Also, strong odors emitted from terpene cleaners may be objectionable to sensitive individuals. Alkaline cleaners are nonvolatile and emit no harmful odors.

Pretreatment
Pretreatment is usually required with both solutions before discharge to a wastewater treatment facility.

Cleaning Efficiency
Both alkaline and terpene cleaners achieved cleaning efficiencies comparable to organic solvents. For heavy grease, wax, and tar, terpene cleaners tended to be the better solvent. However, alkaline cleaners possessed a greater ability for removing inorganic and polar organic soils. In both cases, the use of cleaning enhancements improved the cleaning performance.

Corrosion
When using alkaline cleaners, corrosion during the cleaning cycle was minimal. During testing, aluminum and magnesium exhibited a high tendency for corrosion due to the elevated pH levels. The problem depends on the cleaner formulation and can be controlled. Terpene cleaners are corrosive to elastomers and metals; therefore, careful selection of equipment and parts washed is necessary.

Recycling
The option for recycling is only available for alkaline cleaners. Aqueous terpene cleaners are not recyclable because the contaminants do not physically separate from the cleaner. Ultrafiltration was attempted with terpene cleaners; however, the cleaner destroyed the ultrafilter adhesives and supported materials, making filtration impossible. Ultrafiltration can be used as a recycling option with alkaline cleaners. Preliminary testing should be performed to ensure the cleaner and filter membrane are compatible.

Economic Viability
Compared to Stoddard solvent and TCA, alkaline cleaners provided a more efficient cleaning process at a reduced cost. However, terpene cleaners did not achieve comparable cleaning at a lower cost. Even at various dilutions terpene cleaners were not as cost effective as Stoddard solvent.

7.12 Summary

The nontoxic nature of alkaline cleaners increases the safety and confidence of personnel. Extra equipment (e.g., respirators, increased ventilation, etc.) required with organic solvents is no longer necessary, making the working area a more pleasant environment. An example of this can be seen at the Corpus Christi Army Depot and Aviation System Command. An alkaline cleaner was used as a replacement for an organic solvent in aircraft cleaning operations. In addition to reducing waste, workers did not need to wear as much protective equipment and could work for longer periods of time without experiencing acute toxic effects (e.g., dizziness, fatigue, etc.). The net result was an increase in work efficiency due to the creation of a safer working environment.

Alkaline cleaners have proven to be biodegradable under laboratory test conditions. However, in full-scale operation, the ability of alkaline cleaners to biodegrade tends to be a function of site-specific operating conditions present at the wastewater treatment facility. A compatibility evaluation should be performed at the treatment plant to ensure the cleaner meets all required specifications. Based on the results, modifications to the plant may be necessary before incorporating an alkaline cleaner into the cleaning system.

The overall cleaning efficiency of alkaline cleaners is comparable to organic solvents. Heavy oils and greases have caused problems during immersion cleaning, increasing the cleaning times required for 100 percent removal. In some cases, this problem can be eliminated by installing cleaning enhancements (i.e., ultrasonics, spray washing, etc.) into the process. These process modifications can help reduce the cleaning times, making the system more efficient. Metal corrosion during cleaning has been minimal. Only aluminum and magnesium exhibit corrosion when exposed to alkaline cleaners. But as noted in the literature, certain alkaline cleaners contain chemicals that inhibit this type of corrosion by coating the metal with a protective membrane.

The economic analysis, comparing the degreasers, showed that the replacement of organic solvents with alkaline cleaners is a feasible and cost-effective alternative. In addition to lowering the cost associated with operation and maintenance, liability costs were also considerably reduced due to the cleaner being nonhazardous. As a result, tasks associated with storage, handling, transportation, and disposal are simplified, making the process more efficient.

Aqueous alkaline cleaning systems can be an alternative for degreasing operations at Army installations. Due to the unique operating conditions present at every installation, each system should be thoroughly tested. Preliminary testing will ensure a proper system design that will benefit the installation and the environment. Table 7.7 compares the characteristics of organic solvents and alkaline cleaners.

Table 7.8 summarizes this analysis by showing some of the advantages and disadvantages of aqueous cleaning processes.

TABLE 7.7 - SUMMARY COMPARISON TABLE

	STODDARD	TCA	ALKALINE
SOLVENT TYPE	Petroleum Based	Halogenated	Water-Based
BOILING POINT	300-350 °F	165 °F	212 °F
VAPOR DENSITY (AIR = 1)	5.2	4.6	Nonvolatile
EVAPORATION RATE	0.21	4.6	Nonvolatile
% VOLATILE	100	100	0
% SOLUBILITY IN H_2O	<0.1	<0.1	100
VAPOR PRESSURE (mm Hg)	<0.1	132	0-24
SPECIFIC GRAVITY	0.754	1.32	1.05
FLASH POINT	140 °F	None	None
pH	N/A	N/A	11-130
APPEARANCE	Colorless	Colorless	Varies
ODOR	Kerosene-Like	Ether-Like	Non-Offensive
TLV (ppm)	100	350	None
HEALTH CONCERNS			
Acute:	Skin Irritation	Eyes and Skin Irritation	Skin Irritation
Chronic:	Fatigue, Brain Damage	Headaches, incoordination	None
TOXICITY	Moderate	Moderate	Nontoxic
REACTIVITY	Stable	Moderate	Stable
BIODEGRADABLE	No	No	Yes, Possible System Modification Required
RECYCLABLE	Yes	Yes	Possible With Ultrafiltration
CLEANING EFFICIENCY	Good	Good	Comparable to Organic Solvents
DISPOSAL	Incineration, Fuel Substitution, Sale, Surface Disposal	Incineration and Disposal	Wastewater Treatment Facility
COST ($/GALLON)	4.00	4.00-5.00	11.00-13.00

TABLE 7.8 - ADVANTAGES AND DISADVANTAGES OF AQUEOUS CLEANING PROCESSES

Safety - Aqueous systems have few problems with worker safety compared to many solvents. For example they are not flammable or explosive.	**Cleaning Difficulty** - Parts with blind holes and small crevices may be difficult to clean, and will require process optimization.
Cleaning - Aqueous systems can be designed to clean particles and films better than solvents.	**Process Control** - Solvent cleaning is a very forgiving process. To be effective, aqueous processes require careful engineering and control.
Design Freedom - Aqueous systems allows flexibility in design, formulation, and concentration. This helps provide superior cleaning for a wide variety of contamination.	**Rinsing** - Some aqueous cleaner residues can be difficult to rinse. Some surfactants are especially difficult to rinse. Trace residues may be detrimental for some applications and materials. Rinsing can be improved with deionized water of alcohol rinse.
Removal of Inorganic or Polar Soils - Aqueous cleaning is good for cleaning inorganic or polar materials. Many machine shops are using or converting to water-based lubricants versus oil-based for environmental reasons. These are ideally suited for aqueous processes.	**Drying** - It may be difficult to dry certain part geometries with crevices and blind holes. A piece of drying equipment is often required.
Oil and Grease Removal - Organic films, oils, and greases can be effectively removed by aqueous chemistry.	**Floor Space** - In some cases aqueous cleaning equipment may require more floor space.
Multiple Cleaning Mechanisms - Aqueous cleaning functions by several mechanisms. These include saponification, displacement, emulsification, dispersion, and others. Particles are effectively removed by surface activity coupled with the application of energy.	**Material Compatibility** -Corrosion of metals or delayed environmental stress cracking of certain polymers may occur.
	Water - In some applications high purity water is needed. Depending on purity and volume high purity water can be expensive.

Chapter 8

Conclusions

This study investigated the feasibility of replacing organic solvents with aqueous alkaline cleaners in metal cleaning operations. The data base consisted of a literature review, economic analysis, and research studies performed on alkaline cleaners. Based on the information gathered, the following conclusions are made regarding the use of these cleaners at U.S. Army installations:

- Alkaline cleaners are nonflammable and exhibit no flash point, which makes them ideal candidates for replacement solvents in heated degreasing operations.

- Alkaline cleaners are nontoxic, contain no carcinogenic ingredients, and possess no carcinogenic characteristics.

- Under normal conditions, alkaline cleaners are not reactive and are compatible with most materials. As a result, no special precautions are required for storage and handling, decreasing the Army's liability.

- Pretreatment of spent alkaline cleaning solution is usually required before discharge to a wastewater treatment plant facility. However, in some cases the wastewater can be directly processed at the treatment plant without pretreatment.

- In a laboratory environment, alkaline cleaners are biodegradable. But in full-scale operation, biodegradation depends on site-specific operating conditions at the wastewater treatment plant. Modifications may be required to ensure complete degradation of the cleaner.

- Alkaline cleaners achieve cleaning efficiency comparable to organic solvents.

- Cleaning enhancements, including agitating immersion, spray washing, and ultrasonics, can help improve the cleaning efficiencies for the removal of heavier oil and grease.

- In most cases, corrosion during the cleaning cycle is minimal.

- Because of the high pH of alkaline cleaners, aluminum and magnesium are prone to excessive corrosion. However, this problem is a function of the cleaner formulation and can be controlled.

- Generally, alkaline cleaners are not recyclable. Ultrafiltration can be a recycling option, but preliminary tests should be performed to ensure that the cleaner and filter membrane are compatible.

- The economic analysis comparing alkaline cleaners to Stoddard solvent and TCA shows that cost-effective alternatives exist. Implementing these alternatives can incur savings while reducing the liabilities associated with storage, handling, and transportation.

- Based on the comparison analysis, alkaline cleaners were found to have more beneficial advantages than terpene cleaners. These advantages include no flash point, no toxicity, no carcinogenic ingredients, lower corrosion potential, an option for recycling, and more cost effectiveness.

Appendix A

Alkaline Cleaner Selection Considerations

The U.S. Environmental Protection Agency, realizing the complexity of evaluating an alkaline cleaning system, has developed a guide to outline the alternatives that should be considered during the selection process. The following criteria should be examined when designing an alkaline cleaning system:[20]

I. Organizational

- Compatibility with other corporate goals
- Feasibility given existing organizational structure
- Compatibility with corporate environmental policy

II. Technical

- Chemical cleaning ability
- Physical and chemical characteristics of the cleaning process
- Compliance to specifications
- Material compatibility
- Effect on subsequent processes
- Process control
- Production rate requirements
- Ease of new process installation
- Floor space requirements
- Operating and maintenance requirements

III. Economic

- New equipment costs
- Waste treatment/handling costs
- Costs for permit changes for new construction or new operating procedures
- Operation and maintenance costs including raw materials, labor, and utilities

IV. Environmental, Health, and Safety

- Compatibility with appropriate Federal, state, and local regulations
- Compatibility with regulatory trends
- Public perceptions
- Energy efficiency
- Effects on emissions, effluents, and wastes generated
- Toxicity and worker safety
- Flammability

Appendix B

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