Danaher Tool Group, Springfield, Massachusetts

Nitric Acid Recovery Using Diffusion Dialysis

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The Toxics Use Reduction Institute
Cleaner Technology Demonstration Sites Program

The Toxics Use Reduction Institute
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The Toxics Use Reduction Institute is a multi-disciplinary research, education, and policy center established by the Massachusetts Toxics Use Reduction Act of 1989. The Institute sponsors and conducts research, organizes education and training programs, and provides technical support to promote the reduction in the use of toxic chemicals or the generation of toxic chemical byproducts in industry and commerce. Further information can be obtained by writing the Toxics Use Reduction Institute, University of Massachusetts Lowell, One University Avenue, Lowell, Massachusetts 01854.

Preface

In its 1996 fiscal year, the Massachusetts Toxics Use Reduction Institute launched the first Cleaner Technology Demonstration Sites Program. The goal of the program was to promote the adoption of cleaner technologies by Massachusetts industry. Five companies were selected as demonstration sites to showcase the implementation of technologies that embrace the concepts and principles of toxics use reduction. The program, which included a series of visits to the facilities and related presentations and publications, allowed individuals and firms to observe and assess their value first-hand. Site visits were open to industry, environmental groups, community groups, the media and others.

Associate sponsors of the program included the Massachusetts Office of Technical Assistance for Toxics Use Reduction, the Executive Office of Environmental Affairs, the Department of Environmental Protection, the Environmental Protection Agency of New England, and the Associated Industries of Massachusetts.

This was the first of an annual program allowing a broad range of companies to showcase cleaner technologies. The program will continue to provide grants to recognize the many companies across the Commonwealth that have used toxics use reduction and cleaner technologies while enhancing their firm's competitiveness.

The following report is an in-depth analysis of the cleaner technology(ies) demonstrated at Danaher Tool Group, Springfield, Massachusetts.

Notice

Table of Contents

1.0 INTRODUCTION

Danaher Tool Group, operating under SIC Code 3423, is a manufacturer of high quality steel ratchets for a variety of distributors. The cleaning of racks used in the electroplating process requires the use of nitric acid, a toxic chemical listed under the Toxics Use Reduction Act (TURA). As a result of toxics use reduction (TUR) planning, Danaher Tool Group implemented nitric acid recycling using an integral diffusion dialysis system in its Springfield, MA facility in 1994. Nitric acid can cause injury to plant personnel through inhalation, ingestion, or skin contact. The implementation of the diffusion dialysis system has reduced worker exposure, operating costs, and environmental impact. This report illustrates the successful implementation of diffusion dialysis technology including technical and economic feasibility.

2.0 TECHNOLOGY DESCRIPTION

2.1 Electroplating Process

The main steel components of the ratchets are either forged in-house at Danaher or furnished by external vendors. These forged components then receive a nickel and chrome plate to prevent corrosion and enhance appearance. The electroplating process entails securing the tools to stainless steel racks that conduct electric potential to the secured tools. Most of the surface area of the rack is covered with a plastic insulated coating so that the racks themselves don't attract nickel and chrome ions, but the tips of the rack are left exposed so that electric current can pass through the tools which are attached there. The rack, and thus the tools, receives a cathodic (negative) charge and is submerged in an anodic (positively charged) metal bath. When the loaded racks are submerged in the anodic nickel bath, nickel cations are attracted to and accumulate on the cathodic tool surface. Following the nickel plating operation, the racks holding the secured tools are passed through a chrome electroplating bath where chromium cations are attracted to the tool surface. Upon completion of the plating cycle, the hand tools are removed from the rack, sent to inspection, and the racks are reloaded with a new set of tools for the plating cycle. This process cycle is shown in Figure 1.

After five plating cycles, the exposed tips of the holding racks become heavily plated and no longer transfer their cathodic potential to the secured tools efficiently, which results in a cosmetically rejected part. In order to maintain the functionality of the racks, they are submerged off-line in an acid bath to remove the accumulated chrome and nickel plating. The racks are submerged in a 400 gallon stripping tank of 75% nitric acid (HNO_3) by volume for ten minutes to accomplish this plating removal. Over a period of time, this nitric bath becomes saturated with chrome flake and dissolved nickel and is no longer effective for stripping.

Finished product quality suffers if the contaminant concentration of the stripping bath is not kept at a minimum. Cosmetic reject rates of up to 4% were partly traced to poorly stripped, non-conductive racks. Efforts to decrease rejects through the use of a cleaner, more effective stripping bath led to the dumping of the acid bath more frequently. Historically, the contents of the saturated stripping bath were shipped off-site for disposal as hazardous waste. Danaher realized that extension of the acid bath's service life would be a safer, more cost-effective, and environmentally friendly manner with which to resolve these quality issues.

Danaher's toxics use reduction planning resulted in the installation of a diffusion dialysis system in May of 1994. Through in-process recycling, diffusion dialysis restores the functionality of the stripping acid and dramatically increases its service life, resulting in annual reductions in nitric acid use.

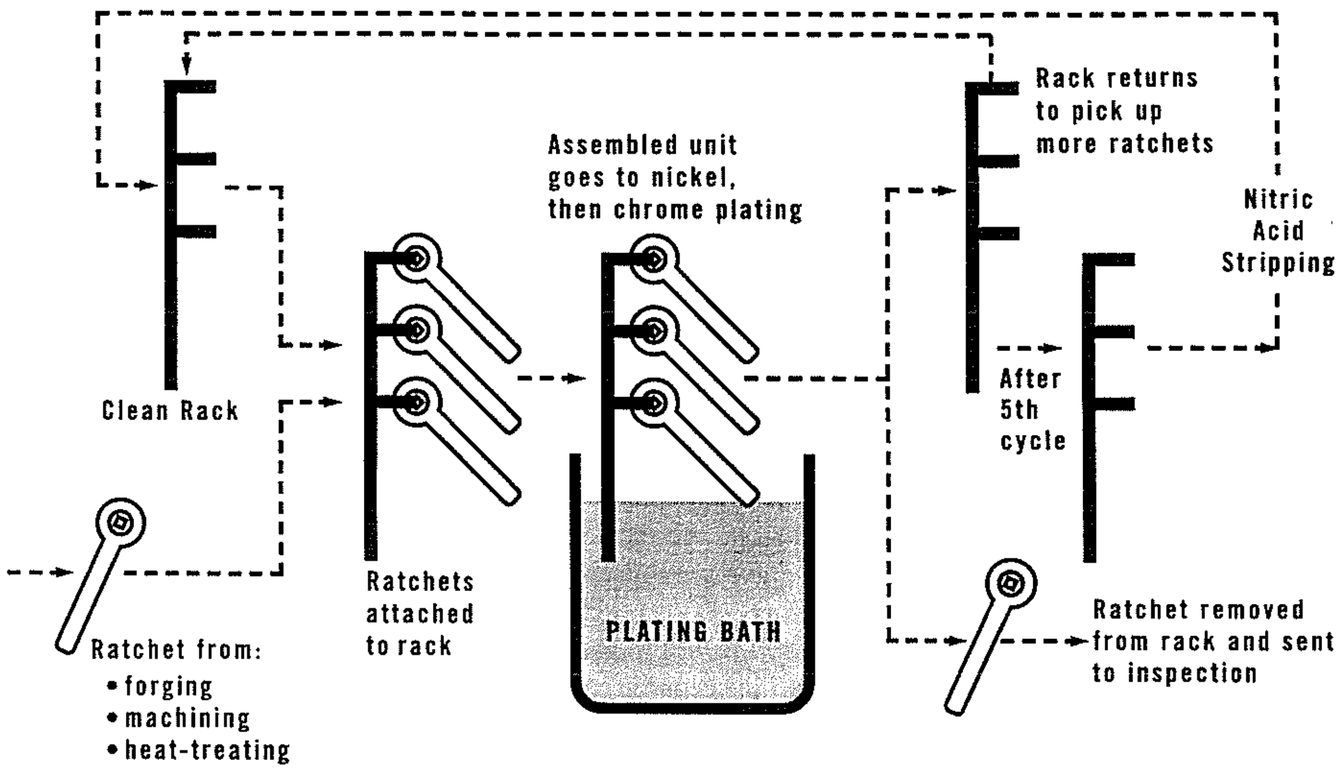
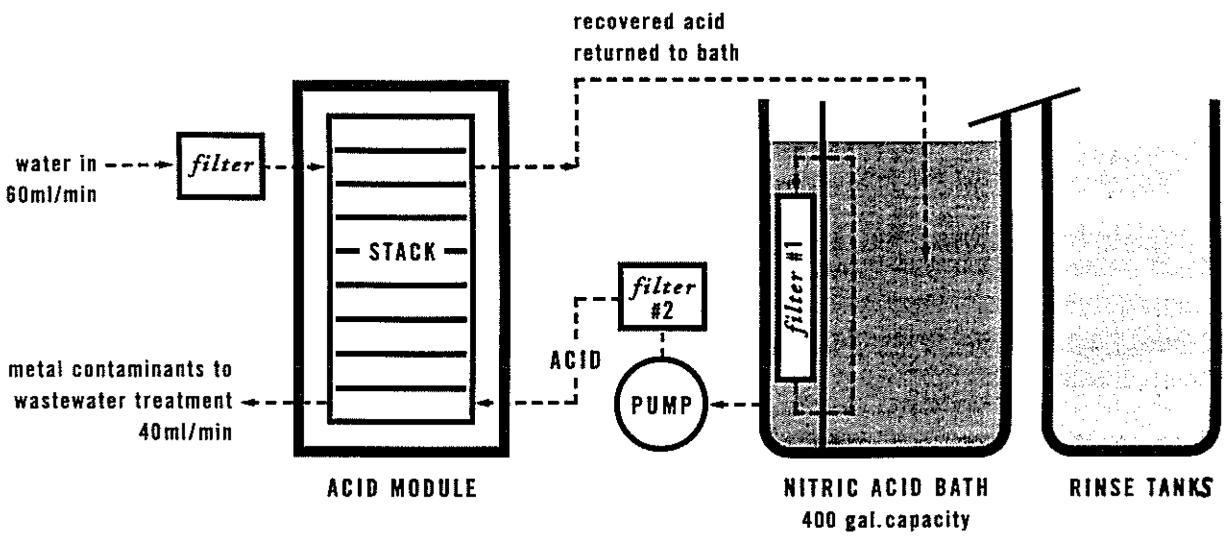


Figure 1 - Plating and Stripping Cycle

2.2 Filtration and Diffusion Dialysis

Once five plating cycles have been completed using a given rack, the rack is dipped into a nitric stripping bath and then two rinse tanks. The stainless steel composition of the rack prevents its acid degradation. The stripping solution, 75% by volume (8.0 Normal) HNO_3, dissolves the nickel into solution causing the chrome plating to flake off the exposed tip (chrome does not dissolve in nitric acid). In order to separate the chrome flake and the dissolved nickel from the bath for acid reuse, the stripping solution is subjected to the recovery system illustrated in Figure 2.



- 5 gal/wk fresh nitric acid added to bath to compensate for drag out
- filter #1 changed once a week
- filter #2 changed once a month

Figure 2 - Acid Filtration Recovery System

The contents of the stripping bath flow through a polypropylene 10 micron *FloKing* filter in a reservoir built into the side of the tank. This filter was added to assure the removal of chrome flakes from the bath so that they don't interfere with the diffusion dialysis process. These filters are changed weekly, when they are backflushed and neutralized at wastewater treatment and then disposed of. The addition of this in-tank filtration unit required a larger stripping tank to compensate for the volume of the filter reservoir and a larger capacity ventilation system to accommodate this larger stripping tank.

Repeated failure of the solenoid unit which regulates water intake caused overflow problems, requiring the installation of a filter on the water feed line into the dialysis unit to avoid interference from solids in the water supply. The filter used is a standard household water filter that must be replaced every 12 months at a cost of $40.

From the in-tank filtration reservoir, the acid and dissolved nickel flow through a second 10 micron filter and into a diffusion dialysis unit manufactured as Model No. AJ-20 by Pure Cycle Environmental Technologies, Inc. The unit consists of a series of anionic copolymer membranes positioned to separate counterflowing spent acid and clean water streams. This membrane separation process allows the diffusion of ions from the acid stream into the counterflowing clean water stream (see Figure 3). The anion exchange membrane has a positive charge and thus attracts the nitrate (NO_3^-) portion of the nitric acid towards it. The concentration gradient between the clean water stream and the spent acid drives the migration of these nitrate ions through the membrane. Since only electrically neutral molecules will be accepted by the clean water stream, the nitrate ions electrostatically attach themselves to hydrogen ions (H^+) which are distributed throughout the solution and migrate as a unit through the membrane. These molecules then dissociate into hydrogen and nitrate ions which comprise the reclaimed acid stream. The counterflowing action of the streams ensures a significant concentration gradient throughout the dialysis unit. Thirty one of these membranes are configured to ensure a stream flow long enough for sufficient migration to reach the desired process efficiency. Figure 4 shows a three cell-pair configuration. The metal cations, such as nickel, are repelled from the anion exchange membrane and are too large and slow moving to pass in any significant quantity through the membrane, but are also under the influence of a concentration gradient, and thus some nickel does pass through. This system has extremely low maintenance requirements. With the exception of early problems with chrome flake perforating several membranes, there has been no need for replacement membranes in the diffusion dialysis stack.

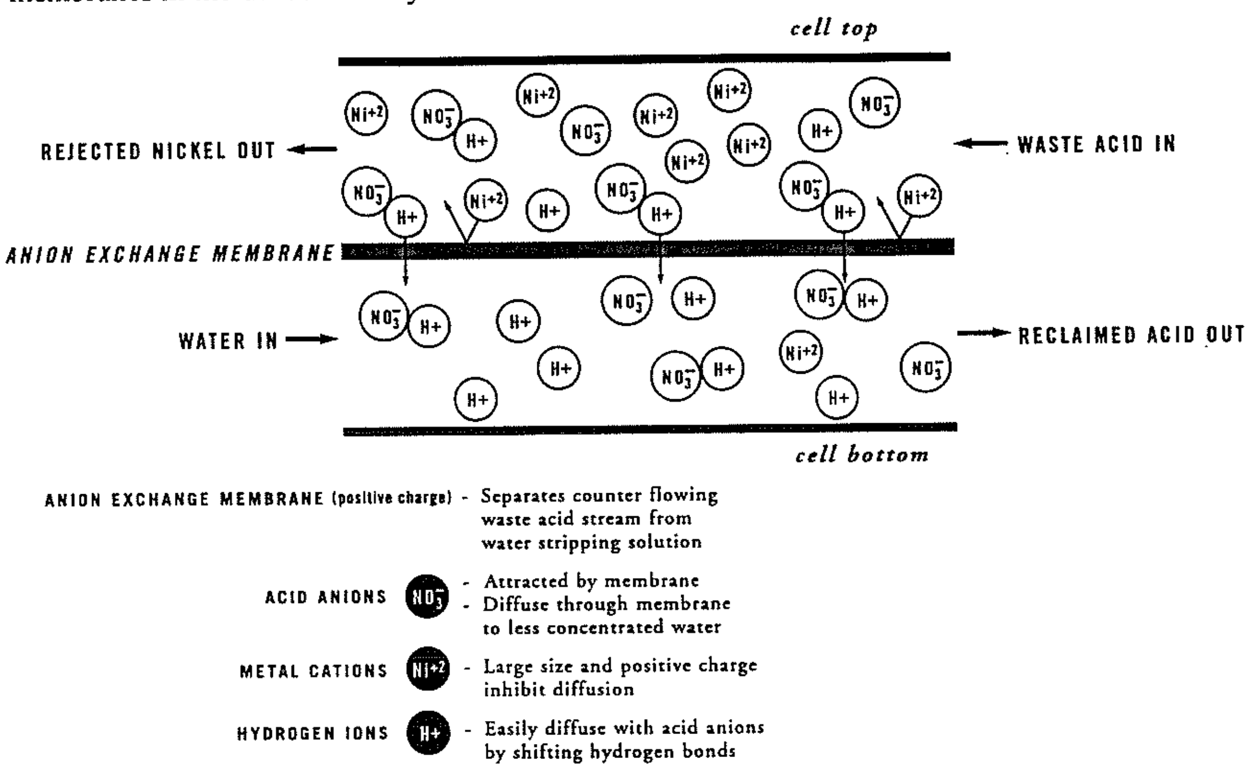


Figure 3 - Diffusion Dialysis Mechanism

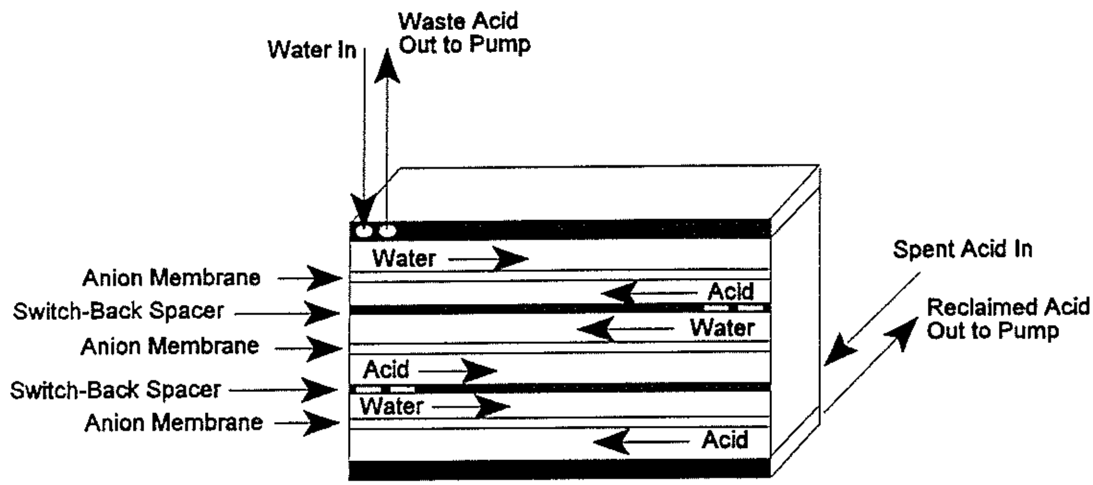


Figure 4 - Diffusion Dialysis Stack, Three Cell-Pairs

The reject solution from the diffusion dialysis unit is directed to on-site wastewater treatment while the recovered acid solution, at an approximate concentration range of 6.0 - 7.5 Normal, flows directly back into the acid bath. Approximately 80% to 95% of the acid is recovered and 60% to 70% of the nickel is removed. This efficiency level is due to the fact that some of the nickel content in the spent acid will breach the membrane and not all of the nitrate/hydrogen ions will migrate through the membrane from the spent acid. This increase in metal ion concentration is a factor in the reduction of solution normality from the required minimum value of 6.5 N. Figure 5 shows an example of the relative levels of nickel and nitric acid of the three acid streams: initial acid, reclaimed acid, and waste acid.

The slower the flow rate through the diffusion dialysis unit, the more thorough the separation, but also the more metal ions will tend to pass through the membrane. An optimal flow rate must be identified to meet these constraints. At Danaher, both the spent acid stream and the recovered acid stream are pumped through the unit at a flow rate of approximately 15 gallons/day, the rate identified as optimal for acceptable recovery of the bath.

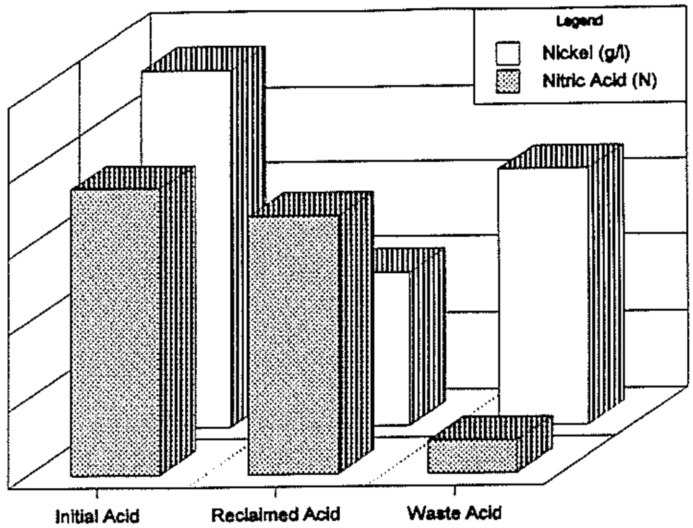


Figure 5 - Nitric Acid & Nickel Levels in Acid Streams

Improvements in process bath quality which have resulted from pilot scale through production operation of this system are characterized in Table 1. In order to maintain the desired process normality of 7.0 N to 9.0 N, approximately 10 gallons/week of fresh acid is manually added to the stripping bath to compensate for losses due to spent acid effluent, from drag-out at the rinse tanks, and recovery efficiency of the diffusion dialysis unit. To further compensate for these losses, the flow rate of the reclaim (incoming water) stream is run slightly higher than that of the reject (spent acid) stream.

The diffusion dialysis process will not perform satisfactorily if the stripping solution is saturated with metals. Since it may take up to two days for the unit to reach the steady-state required for efficient operation, the process must be run constantly to prevent this occurrence. Saturation state may still be inevitable at the initial start-up of the unit or during performance testing, while the concentration of the metal ions in the bath increase to a certain point and then level off until steady state concentrations are achieved.

Table 1
Process Bath Quality - Pilot Scale to Production

		Process	Reclaim	Reject
Pilot Testing	Acid	5.6 N	4.5 N	0.3 N
	Nickel	54.3 grams/liter	7.4 grams/liter	24.1 grams/liter
Production	Acid	7.5 N	6.75 N	0.85 N
	Nickel	9.4 grams/liter	4.0 grams/liter	6.7 grams/liter

3.0 ENVIRONMENTAL & OCCUPATIONAL HEALTH ASSESSMENT

The reduction in acid usage due to the installation of integral recycling has had positive environmental and occupational health impacts. During the year prior to the installation of the diffusion dialysis acid recovery system, Danaher Tool Group used approximately 15,000 lb. of nitric acid, which when spent, was shipped off-site as hazardous waste. With the implementation of the dialysis recovery unit, nitric acid usage for this production unit has decreased to approximately 6,900 lb./yr. representing a 54% reduction in toxics use (See Table 2). Byproduct generated from this process was approximately 15,000 lb. in the year prior to the installation of the diffusion dialysis unit (1993). A reduction in byproduct to approximately 6,700 lb. of nitric acid at the end of the first year resulted in a Byproduct Reduction Index (BRI) of 50.6%.[1] An estimated reduction in byproduct to 3,745 lb. by the end of the second year resulted in a BRI of approximately 71%. This byproduct stream is sent to wastewater treatment, neutralized and then discharged to the local publicly owned treatment works (POTW). The emissions reduction index (ERI) from 1993 to 1995 has been 100.0% signifying a complete elimination of off-site shipments of spent nitric acid as hazardous waste. These reductions translate to reduced worker exposure, less probability of spillage, and fewer hazards from the manufacturing process.

Table 2
Annual Nitric Acid Usage

Year	Nitric Acid (lb.)		Production (# Racks)	Comment
	Use	Byproduct		
1990	10,404	10,404	n/a	Begin TUR reporting; no rack monitoring
1991	7,514	7,514	n/a	10 week labor dispute; low production year
1992	16,184	16,184	n/a	Begin QA/QC measures; dump nitric bath more frequently
1993	15,028	15,028	132,106	Begin phaseout of accessories; resulting in use of fewer racks
1994	12,396	6,689	119,116	Implement acid recovery system; May 1994
1995	6,936	3,745 (estimated)	114,720	Nitric acid usage below 10,000 lb. reportable threshold

[1] BRI is calculated according to the formula 100 × [(A−B)÷A], where:
A = byproduct generated in the base year ÷ unit of product generated in the base year
B = byproduct generated in the reporting year ÷ unit of product generated in the reporting year

Due to the dramatic reduction in nitric acid consumed annually and the reduction in acid bath changeovers since implementation of the acid recovery system, worker handling and exposure to nitric acid has been considerably reduced. Since the acid replenishment of the bath is conducted manually, the annual reduction correlates directly with reduction in worker exposure through skin and eye contact or inhalation.

4.0 ECONOMIC ASSESSMENT

The TUR efforts of Danaher Tool Group have brought a positive economic value to plant operations in addition to the positive environmental and occupational safety impact. The capital investment in the acid recovery system allowed Danaher to increase the capacity of the production unit for additional added value. Table 3 illustrates the operating costs and savings associated with the implementation of the acid recovery system. The savings are in the form of reduction in nitric acid usage, reduction in hazardous material disposal costs, and elimination of TURA reporting and compliance costs for nitric acid, while operating costs include water, filters, and electricity. Labor costs associated with dumping the bath every three month have been eliminated, as well as any costs which may be incurred from handling and spillage accidents.

Table 3
Annual Operating Costs - 1993

Savings	
Nitric Acid	$2,761
Hazardous Waste Disposal	$3,200
TURA fees	$1,100
Costs	
Water, Filters, Electricity	($217)
Net Savings	$6,844

The capital costs associated with this acid recovery system include the diffusion dialysis unit, installation of a larger volume stripping tank and larger capacity ventilation system, a filtration reservoir, a water filter to protect the solenoid unit which regulates water intake, and the associated plumbing and electrical installations. The costs of these accessories are included in the capital expenditures in Table 4. An additional $4,500 in deposits for stainless steel barrels has been eliminated from the cash flow for this process. When operating and capital costs are considered, the payback for the acid recovery system was calculated to be 2.1 years.

The cosmetic rejection rate of plated tools was reduced to less than 1% with implementation of the quality assurance and quality control measures which included a clean stripping bath. Though these measures resulted in labor and material savings, they are difficult to isolate and quantify, and therefore have not been accounted for in the calculations.

Table 4
Capital Expenditures & One-Time Costs

Item	Cost
Pure Cycle AJ-20 Acid Recycling System	$15,800
Increased Capacity Tank	$987
Modified Ventilation System	$4,230
Filter Reservoir	$1,473
Flo-King Filter model BX-1200-8	$460
Electrical/Plumbing	$1,000
Barrel Deposits	($4,500)
Total	$28,450

5.0 RESOURCES AND BARRIERS

The TUR efforts at Danaher Tool Group were greatly facilitated by the support of management and the involvement of all levels of the work force in decision-making. In addition, Danaher was encouraged to pilot test the technology after seeing it demonstrated successfully at another facility.

Management encouraged the development of a closed-loop production unit for the stripping operation, resulting in engineering personnel taking special notice of an article about the closed-looping of a similar operation at a plating job shop in Chicopee, MA. This article led to interaction with Pure Cycle Environmental Technologies, a manufacturer of diffusion dialysis equipment similar to that used at Danaher. Though the operators were skeptical at first with the change in their work flow, they are now comfortable with the new process and its low maintenance requirements.

Pure Cycle Environmental Technologies conducted pilot scale testing in 1993 using in-process stripping solution from Danaher. The results of this testing demonstrated the viability of the technology for Danaher's nitric acid bath and prompted the capital expenditure and implementation of the equipment.

Several engineering issues required resolution during the production scale-up of the diffusion dialysis unit, including the unsatisfactory performance of the unit when the stripping solution is saturated with metals. It turned out that this was only a consideration at the initial start-up of the unit and during performance testing, since the solution should never be close to saturation during proper operation. The installation of unexpected equipment such as the larger volume stripping tank and ventilation system was accomplished within the economic constraints of the project. All of these issues were successfully resolved and production operation of the acid recovery system began in May 1994.

6.0 TRANSFERABILITY

Diffusion dialysis units can be used to recover almost any strong acid, such as those used for stripping, cleaning or plating operations. Some examples of acids being reclaimed using diffusion dialysis include nitric acid pickles, nitric acid or MSA (methane sulfonic acid) from tin/lead stripping baths, sulfuric acid anodizing baths, hydrochloric acid baths for chrome stripping, and hydrochloric/hydrofluoric/ferrous chloride baths with aluminum. These and other processes can significantly reduce the quantity of acid used on-site by recovering the acid in-process. Units are available which handle flow rates from under 5 gallons/day up to 1000 gallons/day. The range of sizes and the efficiencies of the units make it appropriate for a wide variety of applications. Diffusion dialysis is a proven method for accomplishing this recovery at a reasonable operating cost, as demonstrated at Danaher Tool Group.