Pilot of the Pollution Prevention Technology Application Analysis Template

Utilizing

Acid Recovery System

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DISCLAIMER

This document pilots the Pollution Prevention (P2) Technology Application Analysis Template (P2 Template) on Zero Discharge Technologies Inc. Acid Recovery System. The document is designed to assist the user in analyzing the application of pollution prevention technologies. While it provides a template for the general types of questions that you should ask when evaluating a P2 technology, it may not include all of the questions that are relevant to your business, or which your business is legally required to ask.

This document is not an official U.S. EPA or Army Corps of Engineers guidance document and should not be relied upon as a method to identify or comply with local, state or federal laws and regulations. EPA and the Army Corps of Engineers has not examined, nor do they endorse, any technology analyzed using this template.

Preface

The Executive Office of Environmental Affairs' STrategic Envirotechnology Partnership (STEP) and the Toxic Use Reduction Institute (the Institute) located at the University of Massachusetts Lowell entered into an Interagency Service Agreement (ISA) to document the utility of the Environmental Protection Agency – New England's Pollution Prevention Application Analysis Template. The Institute enlisted the Gloucester, Massachusetts-based consulting company Greiner Environmental to complete an analysis of the Acid Recovery System marketed by Zero Discharge Systems, Inc.

This analysis of the Zero Discharge Systems, Inc.'s Acid Recovery System is one of four analyses completed for this project. The other three reports are on the following technologies: Serec Vacuum Degreasing system; Suparator® Thin Film Oil Recovery system; and M/A COM Inc's Semi-Aqueous Cleaning System. In addition, two narrative summaries discussing the practical utility of adopting the template approach for pollution prevention (P2) technology analysis have been prepared by Karen Thomas (formerly with the Institute) and Tim Greiner of Greiner Environmental.

For additional information about any of these technologies or technology reports, please contact Paul Richard of STEP at 617-727-9800 or for information about the P2 Technology Analysis Template, contact Abby Swaine of the Environmental Protection Agency – New England at 617-918-1841.

The Institute would like to thank the Executive Office of Environmental Affairs and the Environmental Protection Agency – New England for their financial support of this project. The Institute acknowledges the generous cooperation of Anthony D'Amato of Zero Discharge Technologies Inc.

Introduction

The purpose of the Pollution Prevention Technology Application Analysis Template is to assist potential users in evaluating the applicability of innovative pollution prevention technology. In addition, the template is designed to assist vendors of pollution prevention technologies in developing their own technology application analyses. This template is not intended to suggest that a vendor should limit the information provided to a potential user of a pollution prevention technology. Any additional information beyond that suggested in this template may be useful and should be made available.

This technology application analysis characterizes the main features of the Acid Recovery System manufactured by Zero Discharge Technologies. The Acid Recovery System uses Diffusion Dialysis Membrane Technology to effectively recover and reuse mineral acids such as Nitric, Hydrofluoric, Hydrochloric, Phosphoric, and Sulfuric Acids. The system can be used in either batch or continuous modes. The Acid Recovery System recovers acids from various metals plating operations including:

- Acids from rack stripping, rework stripping and tank passivation
- Acid from aluminum anodizing, steel pickling, or metal etching
- Acid from electro-polishing and bright dipping
- Acid from stainless steel and titanium pickling
- Acid from metal cleaning baths and cation exchange regenerant solution

This report presents four full scale applications, including benefits, costs associated with implementation, regulatory aspects, and lessons learned from the application experience.

The acid recovery system is suitable for a variety of acids and acid mixtures with metal cation contaminants and is not limited to those encountered in metal plating alone.

NOTE: The designation “P2” is used for “pollution prevention” throughout this document

Contents

Description of Acid Recovery System

Acid baths in metal plating shops routinely become contaminated with a high concentration of metal ions, as a result of the reaction between the acid and metal substrates. Typically, companies slowly bleed metal-contaminated waste-acids into their wastewater. However, most of the time, these waste-acids are not exhausted, rather the high concentration of metal ions causes the acids to lose their effectiveness. Zero Discharge's Acid Recovery System uses a principle called Diffusion Dialysis to recover acids by removing the metal contaminants. Diffusion Dialysis employs a semi-permeable membrane and counter-current flow to separate the acids from the metal contaminants. The following section describes the Acid Recovery System and Diffusion Dialysis technology in greater detail.

Technology Description

Overview

The Acid Recovery System uses Diffusion Dialysis Membrane Technology to effectively recover mineral acids for reuse. Diffusion Dialysis is a phenomenon in which a solute travels from an area of high concentration to an area of low concentration through a semi-permeable membrane. Solutes can be separated from each other by the differences in their diffusivities, their molecular size, and their charge.

A Diffusion Dialysis system for the recovery of mineral acids utilizes an anion exchange membrane positioned between two solution compartments. One compartment contains the contaminated acid solution while the other compartment contains de-ionized water.

The disassociated acid radical diffuses through the anion exchange membrane into the de-ionized water compartment. The hydrogen ion associated with this acid radical will also readily pass through the membrane because of its small size and mobility. The metal cations are repelled by the membrane and do not diffuse through it.

The driving force for the ionic transport is the concentration gradient across the membrane. The diffusion of acid will occur until the law of electro-neutrality is satisfied. By continuously flowing the solutions counter-current, the law of electro-neutrality is never satisfied, and acid continuously diffuses through the membrane.

These membranes are placed into a membrane stack and are separated by hydraulic spacers. Typically the flat membranes are placed in a vertical position and both the contaminated acid and the DI water are pumped into the membrane stack. The problem associated with the vertical configuration is that the air dissolved in the water is liberated inside of the membrane stack. This air will continue to collect and bind the face of the membrane, resulting in inefficient use of the membrane surface area. In these systems the recovered acid must be pumped backwards through the membrane stack to liberate the gas. This results in wasted acid due to the inefficient operation of the system. Zero Discharge's improvements on the vertical configuration incorporate membranes stacked horizontally. This allows the gas to flow across the membrane so it is easily liberated.

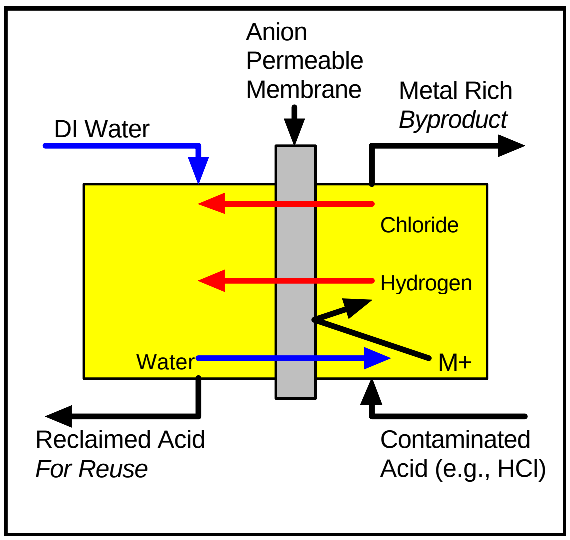
One of the problems associated with pumping this air/gas mixture is that the solution flow is periodically stopped because of a vapor lock. This causes the build-up of pressure within the membrane stack, which eventually ruptures the membranes. Zero Discharge's design incorporates positive displacement pumps, which draw or suck the solution through the membrane stack. The positive displacement pumps pulse so that they shock the gas into dislodging from a vapor lock position. Also, if a vapor lock does occur, the pumps cannot create enough of a vacuum to damage the membranes.

For the design of the Diffusion Dialysis system, Zero Discharge has been granted two patents -- they are U.S. Patent Nos. 5,217,612 and 5,445,737.

Detailed Description

Feed acid and water are pumped through filters into 2 feed tanks elevated 2-3 feet above the membrane stack. These tanks are equipped with liquid-level controllers to automatically fill the tanks as the level drops. The feed acid and water flow by gravity to the inlet ports of the membrane stack. The suction end of two positive displacement diaphragm pumps are connected to the outlet ports of the membrane stack. The feed acid solution and the water are drawn through the membrane stack at constant flow rates. As the two solutions flow in opposite directions across the membranes, the acid passes through the membranes and is collected in the water stream. [See Diagram 1 below.]

Diagram 1



The water stream exits the membrane stack containing up to 95% of the original acid in the feed acid stream while contaminated with as little as 5% of the metals in the feed acid. This constitutes the Recovered Acid, which is then either pumped into a holding tank or directly back to the process tank. The feed acid exits as the reject stream and contains as much as 95% of the original metals and as little as 5% of the original acid. This stream can either be pumped to a holding tank or directly to waste treatment.

Recovering the acid can result in up to a 92% reduction in acid consumption for the process bath. The metal rich reject/waste stream is much less hazardous to treat and can result in up to an 89% reduction in waste treatment chemical usage and a decreased potential exposure to hazardous materials by waste treatment operators.

It is important to note that, because equal volumes of waste acid and de-ionized water flow into the system, the reject stream is equal in volume to the waste acid that would previously have been disposed. However this stream can be reduced in volume (by evaporation or other means), sent for metals recovery, or treated using fewer chemicals than the waste acid. A significant benefit in cost savings from the Acid Recovery System versus treatment is realized in reduced virgin acid purchases.

Technology Applicability

This section describes the applicability, the development history, and the advantages and limitations claimed by the technology vendor.

Applicability to Industry/User

The Acid Recovery System can be applied to almost all mineral acids including: hydrochloric, nitric, sulfuric, and mixtures of these acids. This technology recovers these acids when used for hydrochloric pickling, sulfuric acid pickling, nitric acid rack stripping of nickel and copper, nitric acid stainless steel passivating, sulfuric acid anodizing, and most other operations where cationic contaminants are found. Benefits of the system for most users include: reduced acid consumption, reduced waste treatment and disposal, process optimization via bath stabilization, enhanced metal recovery ability, reduced labor costs, reduced reporting requirements, and reduced liability. A limitation of the system is the degradation of the membranes when exposed to strong oxidizing environments such as chlorine, hydrogen peroxide and hexavalent chrome.

This system can be either operated in a batch or on-line (continuous) configuration. In the batch configuration, the entire acid process bath is taken off-line and pumped to a holding tank. This acid is processed through the Acid Recovery System and the recovered acid is collected in a holding tank. Once the entire bath is processed, the entire volume is exchanged with a contaminated acid process bath, which then undergoes the recovery procedure.

When operated on-line, the process tank acts as the holding tank. Acid is removed directly from the process tank, flowed through the Acid Recovery System, and the recovered acid is pumped directly back to the process tank.

Operating in the batch configuration requires a smaller sized system, creates less acid waste, and requires less waste treatment chemicals. Operating the system on-line requires a larger system because the metals concentration in the feed acid is less than in the batch configuration. Advantages of the on-line configuration are:

- No need for installation of the feed acid and recovered acid holding tanks.
- Improved parts processing performance because the metals concentration is held constant.
- No need to pump acid between the holding tanks and the processing tank.
- Reduced operator exposure of hazardous chemicals.

Development / Application History

Year	Location	Scale	Results
1991, Phase I	Pitney Bowes	Commercial, Nitric Acid Rack Strip of Nickel Hydrochloric Acid Rack Strip of Chrome	No bath dumps, Virgin acid added to replace losses from dragout & dialysis, 92% HCl recovery, 96% Nitric recovery
1992, Phase II	Pitney Bowes	Commercial, Hydrochloric Acid Pickle	HCl baths recovered and reused, 90% HCl recovery,
1992-1993	Lawrence Livermore National Laboratory	Test Lab and Commercial Application, variety of processes and acid baths	79.5% nitric acid recovery, 75.5% HCl recovery. 89.2% and 90.1% recovery of sulfuric acid from two processes
1994	Danaher Tool Group*	Commercial, Nitric Acid Strip	Up to 95% nitric acid recovery, up to 70% reduction in nickel metal
1997	Allied Signal Aerospace	Commercial, Sulfuric Acid from Copper Strip	87.5% sulfuric acid recovery, 81.3% reduction in copper metal

* This unit was installed by PureCycle under license from Zero Discharge Technologies, Inc.

Acid Recovery System Application

The following section describes the use, location within the facility, and effect on plant operations at four application sites -- Pitney Bowes, Allied Signal Aerospace, Lawrence Livermore National Laboratory, and the Danaher Tool Group. (The Acid Recovery System unit installed at the Danaher Tool Group facility was installed by PureCycle, under license from Zero Discharge Technologies Inc.) For application information on these or other application sites contact Anthony D'Amato at Zero Discharge Technologies Inc. (413) 592-4242.

Application

General Setting

Pitney Bowes, Stamford CT

Pitney Bowes is a marketer and manufacturer of mailing and office systems. Part of the company's manufacturing operations includes a metal surface finishing facility, which uses hydrochloric and nitric acids for pickling and stripping. Waste streams of spent nitric acid solutions, heavily contaminated with nickel, were disposed of off site. Spent hydrochloric acid solutions contaminated with chromium, iron and nickel is used as in-house waste treatment for pH adjustment. The unusable hydrochloric acid and bulk metal is disposed of off site as hazardous waste.

The goal of the facility was a three-phase implementation designed to recover spent acid solutions resulting in elimination of waste disposal and downtime due to bath changes.

1. Phase 1 to install dedicated acid-recycling units for: a) hydrochloric acid tank used for chromium stripping, b) nitric acid tank used for nickel stripping
2. Phase 2 to install a centralized acid-recycling system in the waste-treatment area, for bulk hydrochloric acid dumps from pickling operations.
3. Phase 3 to install a dedicated acid-recycling unit for nitric acid electroless nickel stripping.

Preliminary results of pilot studies showed excellent results in removing metallic contaminants, as well as recovering acids with sufficient concentration for continued use.

Allied Signal Aerospace

Allied Signal, Federal Manufacturing & Technologies operates a printed circuit fabrication department. The plating facility maintains five sulfuric acid tanks, generating 29,699 LB/yr. of concentrated acid liquid waste. This waste is treated on-site in their Industrial Wastewater Pretreatment facility yielding 7,000 pounds of hazardous sludge per year. Allied Signal had previously determined that sulfuric acid was the one of the highest volume discharges from the shop. The goal of the facility was to recover a percentage of the spent sulfuric acid and realize a reduction in the industrial wastewater pretreatment facility sludge.

Preliminary results for the system showed an 87.5% acid recovery and an 81.3% reduction in copper contaminant.

Lawrence Livermore National Laboratory

Lawrence Livermore National Laboratory (LLNL) is a US Department of Energy national laboratory operated by the University of California. LLNL applies science and technology, with a focus on global ecology, to increase national economic competitiveness. Under contract with the Department of Energy, the Manufacturing and Materials Engineering Division tested the Acid Recovery System on a variety of acid solutions and mixtures

The goal of LLNL was to test the Acid Recovery System in four controlled settings:
1. Nitric acid solution used to strip aluminum and stainless steel electro-forming mandrels.
2. Hydrochloric acid solution used to de-scale steel and deoxidize copper.
3. Spent electrolytic activation solution containing sulfuric acid.
4. Sulfuric acid anodizing solution. Several bright dipping solutions were also tested.

Danaher Tool Group

Danaher Tool Group is a manufacturer of high quality steel ratchets for a variety of distributors. The components of the ratchets receive a nickel and chrome plate at Danaher. The racks are stripped for ten minutes in a 400 gallon stripping tank of 75% nitric acid by volume. The racks used in the electroplating line begin to lose their ability to transfer electricity to the part after five plating cycles. Eventually the nitric stripping bath becomes saturated with metals and loses its effectiveness. For this reason, Danaher Tool Group investigated acid recovery.

Danaher Tool Group installed a 15 gpd in continuous mode on their nitric acid strip tank. Pilot testing of the acid recovery unit achieved an 80% acid recovery rate and an 87% nickel metal rejection rate. In production use of the acid recovery unit resulted in a 90% acid recovery rate and a 60% nickel metal rejection rate.

Technology Implementation At Industry Plant Site

NOTE: The size of the system is designated by the value: gpd (Gallons Per Day)

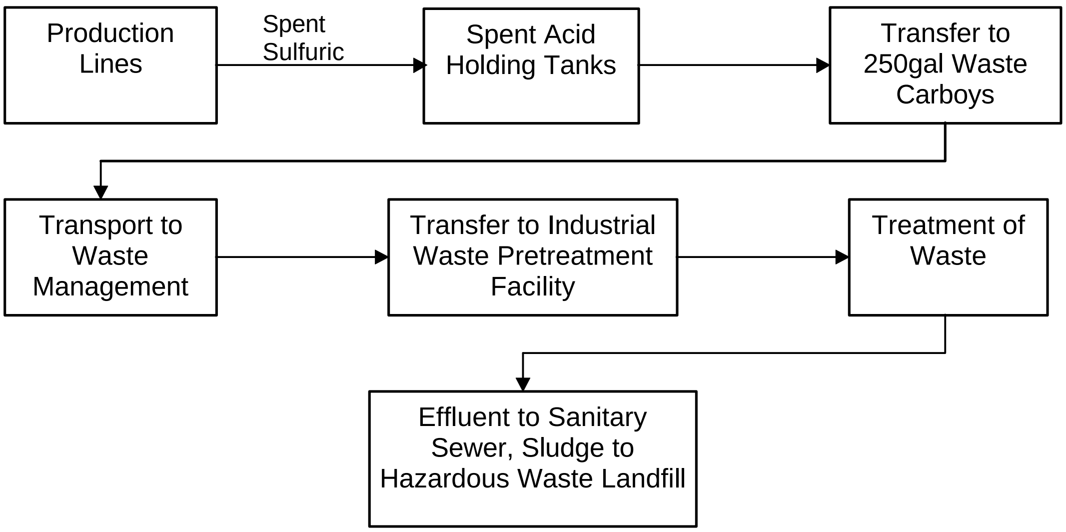
Pitney Bowes:

The 25 gpd and 50 gpd systems installed by Zero Discharge are plumbed directly to their respective acid baths. The 100 gpd system installed in October 1992 by Zero Discharge is located directly below plating department in the waste treatment area. A 1000 gallon tank receives bath dumps from the plating department and is plumbed directly to the recovery unit. A second tank holds recovered acid from the system prior to being returned to production. A third tank receives the reject stream where it is held prior to waste treatment.

Allied Signal Aerospace

The following block diagrams show the traditional technology was used to handle spent sulfuric baths at Allied Signal (Figure 1) and how the process was modified by the installation of the Acid Recovery System (Figure 2).

Figure 1: Sulfuric Acid Waste Process Prior to Acid Recovery System



As shown in Figure 1, the spent sulfuric is transferred several times before ultimately being treated and disposed. Transfers and transportation could potentially cause worker exposure to hazardous material via spills or splashes. In addition, none of the acid is reusable and must be treated with additional chemicals and resources.

Figure 2: Sulfuric Acid Waste Process with Acid Recovery

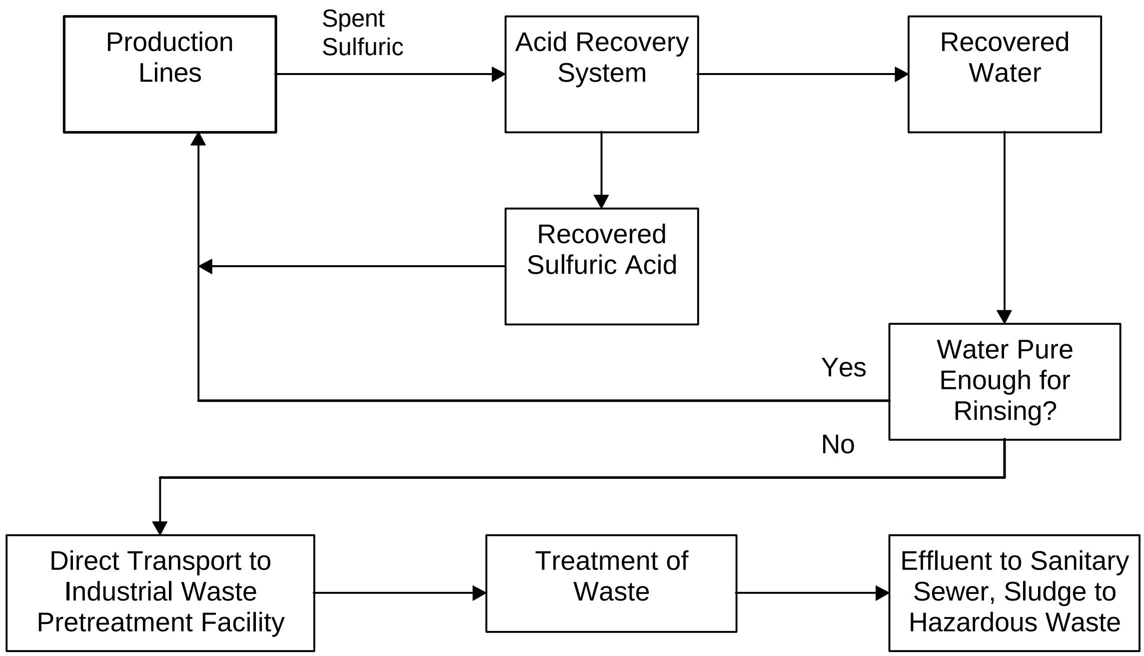


Figure 2 shows the process as modified by the Acid Recovery System. Hazardous material is transferred automatically with pumps from the process to the recovery system. The reject stream is the only component which would require handling if it is not pure enough to be used as a rinse and less handling means less potential exposure.

Lawrence Livermore National Laboratory

The tests were performed at the lab using a small 5 gpd system with an 11 cell-pair stack. The tests of the four process solutions were performed in batch configuration.

Danaher Tool Group

The acid recovery system at Danaher Tool Group consisted of a thirty one cell pair stack operating in continuous mode. The system was plumbed directly to the 400 gallon nitric acid strip tank.

Acid Recovery System Performance

This section presents performance data for the Acid Recovery System as the result of an actual application. The technology's performance in the selected application is described by summarizing the application runs made and the performance achieved.

Performance Goals

The Acid Recovery System is designed to allow the recovery and reuse of mineral acid baths. Reusing the acid baths will

- Reduce the usage of raw materials (source reduction) such as new acid,
- Decrease treatment chemical usage such as sodium hydroxide for acid neutralization,
- Eliminate the need to dispose of spent acid baths to waste treatment
- Potentially allow metals to be recovered,
- Increase process efficiency by allowing greater control over metal concentration in the acid baths
- Increase performance of the acid since operators no longer try to use the bath beyond its useful life.

The recovery performance of a system is dependent upon the type of acid, the acid concentration, the type of metal contaminants, and the metal concentration.

Technology Application Results

Pitney Bowes:

The company's original goal was to achieve zero discharge and this led them to investigate and purchase three acid recovery systems. The first system was a 25 gpd system installed on a 250 gallon tank of hydrochloric acid used for chrome-stripping. Prior to acid recycling, the tank was dumped every six weeks. After installation, the following benefits were realized:

Performance of Acid Recovery System on Hydrochloric Acid			
Parameter	**Initial Acid prior to recovery**	**Recovered Acid**	**Reject Stream**
HCl	4.7N	4.3N	0.4N
Cr	900ppm	200ppm	700ppm
Fe	1700ppm	400ppm	1300ppm
Acid Recovery Efficiency		91.50%	
Chrome Elimination Efficiency		77.80%	
Iron Elimination Efficiency		76.40%	

Also, a 50 gpd system was installed on a 250 gallon tank of nitric acid used for nickel stripping. Prior to the installation of this system, the bath had been dumped every three to four weeks. The system achieved the following results:

Performance of Acid Recovery System on Nitric Acid			
Parameter	**Initial Acid prior to recovery**	**Recovered Acid**	**Reject Stream**
HNO3	9.8N	9.4N	0.4N
Ni	1500ppm	200ppm	1300ppm
Fe	300ppm	100ppm	200ppm
Cu	2000ppm	500ppm	1500ppm
Acid Recovery Efficiency		95.90%	
Nickel Elimination Efficiency		86.60%	
Iron Elimination Efficiency		66.50%	
Copper Elimination Efficiency		75.00%	

The third system purchased from Zero Discharge was, a 100 gpd acid recovery system installed on a hydrochloric acid bath used for pickling. This system was able to achieve the following results:

Performance of Acid Recovery System on Bulk Hydrochloric Acid			
Parameter	**Initial Acid prior to recovery**	**Recovered Acid**	**Reject Stream**
HCl	3.7N	3.3N	0.4N
Cr	500ppm	100ppm	400ppm
Fe	2200ppm	600ppm	1600ppm
Acid Recovery Efficiency		89.20%	
Chrome Elimination Efficiency		80.00%	
Iron Elimination Efficiency		72.70%	

These systems were able to allow Pitney Bowes to take a large step toward achieving their goal of zero discharge by eliminating the frequent bath dumps that were previously necessary. The systems also allowed for savings in acid purchases, treatment, and disposal costs. (See the following section on Cost Information.)

Allied Signal Aerospace

Allied Signal's goal was to significantly reduce the sulfuric acid waste generated by the Federal Manufacturing and Technologies printed circuit fabrication department. The facility also anticipated a high return on investment (125%).

An Acid Recovery System was installed at Allied Signal Aerospace for use on sulfuric acid copper strip tanks. Initial testing resulted in an 87.5% acid recovery rate and an 81.3% reduction in copper in the recovered acid. The system was tested further in continuous and batch configurations. The tests showed that, in batch mode, the system could recover the acid bath in 11 hours. This allows the bath to be processed during a weekend shutdown. After batch treating the acid bath used for etch back, the following results were achieved:

Performance of Acid Recovery System on Sulfuric Acid			
Parameter	**Initial Acid prior to recovery**	**Recovered Acid**	**Reject Stream**
H2SO4	9.5% by vol	8.9% by vol	0.6% by vol
Cu	476ppm	42ppm	434ppm
Acid Recovery Efficiency		93.70%	
Copper Elimination Efficiency		91.10%	

Allied Signal anticipates that the system will save about 26,000 kilograms per year in waste liquid concentrate sent to its industrial waste pretreatment facility as well as 7200 pounds per year in industrial waste sludge.

Lawrence Livermore National Laboratory

Test One was performed on a nitric acid solution used to strip aluminum and stainless steel electro-forming mandrels. The effectiveness of the stripping solution had diminished even though the available acid was still high; this made the solution a good candidate for recovery via diffusion dialysis. Batch treating of the solution yielded the following results:

Performance of Acid Recovery System on Nitric Acid			
Parameter	**Initial Acid prior to recovery**	**Recovered Acid**	**Reject Stream**
HNO3	4.9 N	3.9 N	1.0 N
Cu	60 g/L	7.2 g/L	52.8 g/L
Acid Recovery Efficiency		79.5%	
Copper Elimination Efficiency		88.0%	

The reject stream (130 gallons) was evaporated and re-concentrated and processed through the Acid Recovery System again. After all the processing was complete, the metal could be recovered by electro-winning and vacuum distillation.

Test Two was conducted on a hydrochloric acid solution used to de-scale steel and deoxidize copper. The available acid was quite high but the copper in the solution was immersion plating on the steel, which caused problems with the cleaning process. Electro-winning had been attempted on the solution but was unsuccessful because of the large cathodes required and destruction of some of the acid. The Acid Recovery System was able to achieve the following results on the solution:

Performance of Acid Recovery System on Hydrochloric Acid			
Parameter	**Initial Acid prior to recovery**	**Recovered Acid**	**Reject Stream**
HCl	9.4 N	7.1 N	2.3 N
Cu	10 g/L	1.1 g/L	8.9 g/L
Fe	14 g/L	3.1 g/L	10.9 g/L
Acid Recovery Efficiency		75.5%	
Copper Elimination Efficiency		89.0%	
Iron Elimination Efficiency		77.8%	

The reject stream of 110 gallons was re-concentrated by vacuum distillation. It was re-run through the Acid Recovery System, and another 75% of the acid was recovered. Electro-winning of the second reject stream was only partially successful because of the small volume (25 gallons). It is anticipated that metal recovery on a larger volume reject stream would be worthwhile.

Test Three was performed on a spent electrolytic activation solution containing sulfuric acid. The solution had begun to locally etch and pit because of contamination from excess metals, making this solution a good candidate for reclamation. The Acid Recovery System achieved the following results on the acid solution:

Performance of Acid Recovery System on Sulfuric Acid			
Parameter	**Initial Acid prior to recovery**	**Recovered Acid**	**Reject Stream**
H2SO4	6.5 N	5.8 N	0.7 N
Ni	24 g/L	2.6 g/L	21.4 g/L
Fe	14 g/L	3.1 g/L	10.9 g/L
Cr	9 g/L	2.2 g/L	6.8 g/L
Acid Recovery Efficiency		89.2%	
Nickel Elimination Efficiency		91.0%	
Iron Elimination Efficiency		78.0%	
Chromium Elimination Efficiency		76.0%	

After the solution was recovered and adjusted to the original operating concentration, the solution performed as it did when it was new.

Test Four was conducted on a sulfuric acid anodizing solution. The operating concentration of the solution is 1.9 normal, which is too dilute for recovery by diffusion dialysis. Thus, the solution was distilled to 5.1 normal (some dissolved aluminum was removed from the distillation vessel prior to acid recovery). The recovery system achieved the results listed below:

Performance of Acid Recovery System on Sulfuric Acid			
Parameter	**Initial Acid prior to recovery**	**Recovered Acid**	**Reject Stream**
H2SO4	5.1 N	4.6 N	0.5 N
Al	182 g/L	12.1 g/L	169.9 g/L
Cu	7 g/L	.8 g/L	6.2 g/L
Acid Recovery Efficiency		90.1%	
Aluminum Elimination Efficiency		94.0%	
Copper Elimination Efficiency		89.0%	

The recovered acid was diluted to operating concentration with de-ionized water and returned to the anodizing bath. After dilution, the aluminum content was 2.6 grams per liter and the copper was only 230 parts per million.

Lawrence Livermore National Laboratory was able to reuse a variety of acid baths from different process as a result of the Acid Recovery System. In addition, the lab was able to recover metals from the reject stream, which significantly reduced the waste requiring disposal.

Danaher Tool Group

Danaher Tool Group realized that product quality suffers during the plating process 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 by using cleaner stripping baths led to dumping of the acid bath more frequently. The acid bath dumps were previously shipped off-site for disposal. Danaher Tool Group realized that extending the life of the acid bath would be a safer, more cost-effective, and environmentally friendly solution to improving product quality issues.

An acid recovery system was installed on the nitric acid strip tank at Danaher Tool Group's Springfield facility. Pilot testing of the system resulted in a nitric acid recovery rate of 80% and a nickel metal rejection rate of 87%. The system was then installed in continuous mode on the 400 gallon tank and achieved the following results:

Performance of Acid Recovery System on Nitric Acid			
Parameter	**Initial Acid prior to recovery**	**Recovered Acid**	**Reject Stream**
HNO3	7.5 N	6.75 N	0.85 N
Ni	9.4 g/L	4.0 g/L	6.7 g/L
Acid Recovery Efficiency		90.0%	
Nickel Elimination Efficiency		71.2%	

Danaher Tool Group realized significant benefits as a result of the recovery of acid. During the year prior to installation of the acid recovery system, Danaher used approximately 12,500 pounds of nitric acid. After one year of using the system, Danaher's nitric acid use was reduced to 5,700 pounds, which represents a reduction of 54%. Danaher's acid use during the second year was approximately 4,000 pounds, which represents a decrease of 66% over the year prior to installation. Because the waste stream from the system is significantly reduced and less hazardous, Danaher was able to completely eliminate off-site shipments of spent nitric acid waste.

Cost Information

This section presents cost information associated with the design, construction, startup, and operation of the Acid Recovery System. Each company provided the information presented and the costs estimated in current US dollars.

Cost Estimates

Zero Discharge Technologies, Inc. currently uses the following cost estimates for their technology:

- A small frame system varies in size from 20 to 65 gallons per day. Costs for the system increase proportionately from roughly $17,500 (20 gpd) to $31,800 (65 gpd).
- A large frame system (greater than 65 gallons per day) increases significantly in cost because the larger flow requires more membranes, larger pumps, larger holding tanks, and the larger frame. Contact Zero Discharge for cost estimates of systems larger than 65 gpd.
- Operating costs for the system are approximately $.15 per day per system (not including membrane replacement, labor, and maintenance) based on the following parameters: running 2 positive displacement pumps 24 hours per day, 1/5 hp pump to and from holding tank 1 minute per day, and de-ionized water costs.
- Membrane replacement costs (membranes typically last 5 years, see “Lessons Learned”) at $225 per membrane, not including labor and maintenance. The smallest system has 21 membranes, therefore, for small systems, the replacement costs are ~$4,725.

Capital Costs

Pitney Bowes
Capital Costs for Acid Recovery Systems (including 3 units from Zero Discharge and a similar unit from another vendor) $80,500

Allied Signal Aerospace
Capital Costs for (size) Acid Recover System = $10,466
Installation Cost = $8,414

Lawrence Livermore National Laboratory
Capital costs for the 5 gpd 11 cell-pair stack = $9,000

Danaher Tool Group
Capital costs for the 15 gpd 31 cell pair stack = $23,950

Operating Costs

Pitney Bowes
Operating Cost = $2.04 per day or $744.60 per year

Allied Signal Aerospace
Operating cost after system installation = $5,792

Lawrence Livermore National Laboratory

No operating costs are currently available. Labor costs for the operation of the system are estimated to be less than the labor costs for treating the acid in an industrial wastewater treatment facility.

Danaher Tool Group
Operating costs after system installation = $217 per year

Cost Benchmarks

Pitney Bowes
- Chemical and Disposal Savings = $80,000 per year -- due to 95% reduction in purchase of new acid and elimination of disposal costs.
- Payback period =1.02 years or 12.2 months
- Return on investment = 98.0%

Allied Signal Aerospace
- Total Savings $31,485 (Raw materials savings $6682, and disposal cost savings $24,803)
- Payback period = .63 years
- Return on investment = 157%

Lawrence Livermore National Laboratory
Because the system was tested on a variety of process lines and baths, return on investment information is not yet available. The following cost based analysis presents a picture of the savings anticipated by the lab:

Previous Process (Waste Treatment)	Cost ($)	New Process (Acid Recovery)	Cost ($)
Original HCl Bath (70 gallons)	56.00	Original Bath	56.00
NaOH for acid neutralization	15.46	Disposal	7.40
Waste Disposal	80.25	Make-Up added to original bath	8.00
New Bath	56.00		
Total	207.71	Total	71.40

The cost savings resulting from recovering one bath using the Acid Recovery System versus disposing of one bath via waste treatment are $136.31. In both cases, a 70 gallon HCl bath is returned to production.

Lawrence Livermore National Laboratory did not account for the cost of the Acid Recovery System in the above cost-based analysis but estimated that the recovery system and labor is less than the cost and labor of a traditional treatment system. The laboratory also estimated that the resale value of any reclaimed metal was offset by the cost of electricity required to recover it.

Danaher Tool Group
- Total savings for year one = $11,561 (includes savings in nitric acid purchases of $2761, hazardous waste disposal $3200, regulatory compliance fees $1100, elimination of stainless steel barrel deposits $4500.)
- Payback period = 2.1 yrs

Regulatory/Safety Requirements

As long as the system recovers the acid in process, prior to it becoming a waste stream there are no RCRA permitting requirements associated with the system. State, municipal, and local regulations regarding waste acid recycling vary, so check with permit-writers and technical assistance providers before purchasing and installing the system. The list below contains regulations applicable to the Acid Recovery System, the corresponding regulatory authority, and a brief description of how the regulations apply.

Regulation	Authority	Applicability
Occupational Safety and Health Administration	US Dept. of Labor, state	workplace emissions must meet chemical-specific exposure limits
Resource Conservation and Recovery Act	US EPA, state	most systems generate hazardous waste which must be managed and disposed of accordingly

Waste management requirements include identification of the hazardous waste, generator registration with the US EPA, use of a licensed hazardous waste transporter, and compliance with requirements for waste storage, handling and worker training.

Health/Safety Issues

A notable safety feature of the Zero Discharge system is the use of polycarbonate back and sides, as well as clear plastic front doors, which will contain spills and protect operators. The system can be designed with automated pumps, reducing operator exposure during the acid exchange process.

As potential health risks are significantly reduced using this system, each application is unique and health concerns are always present. The potential exists for operator exposure to low pH materials and/or high metals concentration. Follow federal and state regulations for hazardous materials handling e.g. protective eyewear, gloves, clothing etc.

Lessons Learned

Design Issues

Systems over 65 gpd have some special considerations. A larger frame, larger pumps, larger holding tanks, and more membranes are required for systems of this size and larger.

Limitation of the system is the degradation of the membranes when exposed to strong oxidizing environments such as chlorine, hydrogen peroxide and hexavalent chrome.

Implementation Considerations

Membrane Life:

Membrane life is a function of two things, concentration of feed acid and acid type. Acids of higher concentration tend to shorten the life of the membrane, as do acid types that are oxidizers. Membrane life is typically three to five years, depending on the feed acid, with the longest membrane life being eight years on a 30% nitric solution. During the eight years there was only a 5% reduction in recovery efficiency. The shortest life span for a membrane was two weeks when the system was tested on a hydrogen peroxide solution.

Continuous treatment

Initially, the Acid Recovery System installed at Allied Signal Aerospace was desired to be used continuously by up to five process lines. This was to be accomplished by continuously treating a common spent sulfuric holding tank. Because of the large volume of solution and small size of the recovery system the method appeared too slow for continuous treatment. However, after in-house modifications to the system the company was successful in continuous treatment and batch configuration.

Trials at Lawrence Livermore National Laboratory revealed, as with Allied Signal, the time required for processing large volumes of solution proved to be a drawback. This is attributed to the small size of their test system.

Mixed Acid Solutions

Trials at Lawrence Livermore National Laboratory revealed that mixed acid solutions with monoprotic acids (such as HCl) and diprotic acids (such as H2SO4) are difficult to recover. The difference in the number of protons causes the rejection of some of the diprotic acid. A second recovery run may be required to recover more of the diprotic acid. For this reason, bright dipping solutions were not recovered effectively at the lab. Also, it was difficult to mix the solution back to its operating concentrations.

Benefits Derived From Application

- Reduced acid purchases by up to 95%
- Elimination of production downtime associated with dumping and remaking of acid baths
- Reduction of operator contact with dangerous chemicals
- Improved process control and quality because of more consistent baths
- Reduced neutralization requirements savings in treatment chemicals
- Reduction/elimination of hazardous waste hauling and liability
- Reduced SARA reporting requirements
- high enough metals concentrations that allow further metal recycling

Limitations In Application

The diffusion dialysis technology does not work well in the following situations:

- Use of very strong oxidizers such as chlorine, hexavalent chrome, hydrogen peroxide and chromic acid due to rapid deterioration of the membranes.

- Cadmium rack strip solutions using hydrochloric acid. This is because the cadmium ions form an anion complex which is able to pass through the membrane, thus preventing the rejection of the cadmium metal contaminant.

- Mixed acid solutions, with monoprotic acids (such as HCl) and diprotic acids (such as H2SO4) are difficult to recover. For some bright dipping solutions a second recovery run may be required to recover more of the diprotic acid.

- Lawrence Livermore National Lab experimented with using a single acid recovery unit on two different types of acid baths. The Lab found that switching from acid bath to another containing different metallic contaminants (e.g. one bath contained Cu and another Ni) fowled the system membrane. Firms considering using a single unit to purify different acid baths should investigate whether such an application would result in the more frequent cleaning and/or replacement of the membrane.

Impact On Quality

Follow-up inquiries revealed no adverse effect on end-product quality. Application sites indicated an increased performance and quality of the acid because the operators were not trying to use the solution beyond its useful life.