Waste Minimization

A Collaboration Between Lawrence Livermore National Laboratory & the Northern California Association of Metal Finishers

By C.P. Steffani

This report summarizes efforts to date on a collaborative agreement between Lawrence Livermore National Laboratory (LLNL) and the Northern California Association of Metal Finishers (NCAMF). The goals of this program included: (1) establishing a model metal finishing facility at LLNL to assist regional business in acquiring and implementing chemical processing technology, and (2) providing waste minimization consultation and experimentation. The program was sponsored by the Small Business Initiative Program at LLNL.

Phase 1—Introductory

Phase 1 was the introductory phase. A series of meetings were held with the Board of Directors of the NCAMF to outline the resources available at LLNL and to develop projects of interest to the membership of NCAMF. As part of this phase, a presentation was given at one of the monthly meetings of the membership. The Board then conducted a survey of its membership regarding in-house recycling projects of possible interest. This resulted in a listing of five topics of particular interest to NCAMF members. The areas of interest included:

- Muriatic acid pickle
- Chemical film (alodine)
- Nickel acetate anodize seal
- Electroless nickel
- Caustic cleaner (soak and electrolytic)

Because of funding constraints, LLNL could only evaluate three of the above categories: Acid pickle, electroless nickel, and caustic cleaners. Results of these studies are detailed in the Phase 3 section of this report.

As part of the early effort, LLNL personnel reserved and manned a booth at the NCAMF annual vendors showcase. The tabletop exhibit at this November 1993 meeting included a display of technical literature on waste minimization and process substitutions, process capabilities, methods of using the model shop, and staff backgrounds. LLNL also had a booth display at the November 1994 vendors showcase.

Phase 2—Telephone Access

Phase 2 was a telephone access phase. The LLNL dedicated phone line was staffed 10 hr/day. Questions received ranged from process substitution to training availability. Many of these calls resulted in immediate problem-solving, or provided a resource for further investigation. Some of the calls resulted in requests for a tour or for some prototype processing.

Phase 3—Hands-on

The third phase was a "hands-on" period during which projects suggested by the NCAMF membership were conducted. During this phase, owners and employees from requester facilities could come and use LLNL facilities or send their specific solutions to LLNL for recycling demonstrations. The number of solutions on hand for experimentation and the near-zero discharge processing capability at LLNL were the main draws of this phase. During this period, 17 separate tours were conducted.

Several of the projects suggested by NCAMF were worked, including:

- Acid recycling via diffusion dialysis
- Electroless nickel recycling via electrolysis
- Alkaline cleaner recycling via microfiltration

A key goal with these projects was to prove that recycling could be successfully accomplished with commercial equipment that could be purchased for $10,000–$15,000—a price range that is perhaps affordable to the small jobshop plater.

The electroless nickel recycling project was also co-funded by Michael Meltzer of the Environmental Protection Department at LLNL. This timely help allowed us to complete this important project.

Waste Acid Recycling Via Diffusion Dialysis

Inorganic acids are commonly used in surface finishing shops to remove surface scales, produce bright surfaces, strip unwanted metals and/or coatings, and prepare metal surfaces to receive other coatings. These acids can also be used as the electrolyte for coatings produced by electrolytic oxidation, such as anodizing. Sooner or later, the acids become unusable as a result of contamination with metals, the conversion of the hydrogen ion into hydrogen gas, or they become weakened by either dragout or dilution.

The historic way of dealing with these spent acids is to either dilute or neutralize them, and pass them into the rinsewater stream, or precipitate the metal component as a hydroxide filter cake and send the metal-free liquid to the publicly owned treatment works (POTW). The problems with these methods are that a new bath must be made up when the old is discarded, and the cost of treatment chemicals and equipment is high. Because most acids become contaminated with metals before the acid value is completely exhausted, many times more acid is wasted during dilution than is used for precipitation of the metal.

Recycling of the spent acid has been limited to use as an alkaline neutralizing chemical during waste treatment. Diffusion dialysis equipment has provided a way to recover the usable acid and allow separation of the metal component for recovery and sale to refineries. This technique has been made possible by the invention of membranes that are strong enough to withstand low pH solutions and have long life in an industrial environment.

The process places the acid on one side of a semi-permeable membrane with deionized water on the other. The exchange of ions happens when the two liquids seek equilibrium. The membrane prevents the movement of the metal ions and only allows the diffusion of the hydrogen ion. If the contact time is set at the right interval, much of the acid crosses the membrane while the metals remain behind. The technology is similar to that used by kidney dialysis patients when removing waste products from their blood streams.

The basic equipment is fairly simple: A semi-permeable membrane, two metering pumps, deionized water, and some waste acid. After setting up the dialysis equipment, the operator sets the retention time to a preselected value to insure maximum acid recovery or metal rejection, depending on the stream being recovered. The low-acid/high-metal reject can then be sent to an electrowinning unit and the recovered acid can be returned to the processing area.

Various acid solutions and mixtures of acids have been recovered at LLNL using this technology. One drawback is the time involved for recovery of large volumes. The recovery rate is dependent on the size of the membrane diffusion area. A 50-cell pair stack, which retails for about $9,000, will recover about 10 gal/day.

Another drawback is the recovery of mixed acids in which one of the acids is monoprotic, such as HCl, and the other is diprotic, such as H_2SO_4. The difference in the number of protons causes the rejection of some of the diprotic acid. In this case, a second recovery run may have to be performed in order to recover more of the diprotic acid. Another thing to be aware of is the doubling in size of the volume of liquid that is being recovered. The volume of deionized water that receives the waste acid will have to be contended with, but if electrowinning is done, followed by evaporation, this should not present any problems. The following is a compilation of recovery values obtained by using the equipment with assorted waste acid streams.

Nitric Acid Solution For Stripping Copper

Test 1 was a nitric acid solution that was used to strip copper. The stripping rate had diminished, even though the available acid was still high. The following values represent the acid and metal values before and after the recyclying process:

Start
4.9 N nitric acid
60 gm/L copper metal

Finish
3.9 N nitric acid (79.5% recovery)
7.2 gm/L copper (88% rejection)

The reject solution (130 gal) was evaporated and then re-concentrated and reprocessed through the system. After all processing was complete, the metal (60 lb) was recovered by electrowinning and the spent liquor was recovered by vacuum distillation. A small amount of waste was generated from the mixing of the liquor with the accumulation in the vacuum distillation vessel.

High-Acid Solution To Descale/Deoxidize Copper

Test 2 was conducted on a solution used to descale and deoxidize copper. The available acid was quite high, but the copper in the solution was immersion-plating on the steel, causing problems with pre-cleaning. An electrowinning process was attempted to remove the copper, but with little success because of the large cathode area required to reduce the copper to an acceptable level. In addition, some acid was destroyed as a result of the inefficiency of the process. The following figures represent the acid and metal values before and after recycling:

Start
9.4 N muriatic acid
10 gm/L copper metal
14 gm/L iron metal

Finish
7.1 N muratic acid (75.5% recovery)
1.1 gm/L copper (89% rejection)
3.1 gm/L iron (77.8% rejection)

The process generated 110 gal of low-acid/medium-metal-concentration liquid, which was then concentrated by vacuum distillation. It was run through the system again, and another 75 percent of the acid was removed. At this point, the waste volume was only 25 gal, and it was added to the common waste from the vacuum distillation unit and trucked off-site for treatment and disposal. The electrowinning of this concentrated metal was partially successful, but the small volume made it inefficient to recover. If a larger waste stream had been available, it would have been economical to remove the metal and send it to a refiner.

Spent Electrolytic Activation Solution

Test 3 was conducted on a spent electrolytic activation solution. This solution also had a very high acid value, but was degrading because of contamination from excess metals. The following figures represent the acid and metal values before and after recycling:

Start
6.5 N sulfuric acid
24 gm/L nickel metal
14 gm/L iron metal
9 gm/L chromium metal

Finish
5.8 N sulfuric acid (89.2% recovery)
2.6 gm/L nickel (91% rejection)
3.1 gm/L iron (78% rejection)
2.2 gm/L chromium (76% rejection)

After recovery and adjustment to the original operating concentration, the solution again operated as it did when it was new. The waste products (18 gal) were concentrated by vacuum distillation and sent off as waste.

Sulfuric Anodizing Solution

Test 4 was conducted on a waste type II sulfuric anodizing solution. The operating concentration of the solution was too dilute to allow any dialysis, so the solution was distilled to 5 N from its operating concentration of 1.8 normal. The dissolved aluminum was also concentrated and some of it was removed from the bottom of the distillation vessel prior to acid recovery. The following figures represent the acid and metal values before and after recycling:

Start
5.1 N sulfuric acid
182 gm/L aluminum metal
7 gm/L copper metal

Finish
4.6 N sulfuric acid (90.1% recovery)
12.1 gm/L aluminum (94% rejection)
0.8 gm/L copper (89% rejection)

The recovered acid was diluted with DI water and used to replenish

Table 1

Cost-based Analysis of Original Bath

Original makeup			
HCl	$0.80/gal x 70 gal	=	$56.00
Treatment			
NaOH	$0.68/gal x 23 gal	=	15.46
Disposal	$1.85/lb x 43 lb	=	80.25
New Acid			
HCl	$0.80/gal x 70 gal	=	56.00
		Total	**$207.71**

Cost-based Analysis of Original Bath
With Recycled Acid

Original makeup			
HCl	$0.80/gal x 70 gal	=	$56.00
Treatment			
Disposal	$1.85/lb x 4 lb	=	7.40
New Acid			
HCl	$0.80/gal x 10 gal	=	8.00
		Total	**$71.40**
		Savings =	**$136.31**

the anodizing bath. After dilution, the aluminum content was 2.6 gm/L and the copper was only 230 ppm. The waste liquor was added to the common waste from the vacuum distillation unit. The total waste was estimated at 10 gal of liquid and 10 lb of solid waste.

Several bright dipping solutions were tested with the diffusion dialysis equipment. Because of the mix of mono- and diprotic acids, however, a steady recovery rate was hard to estimate. By using a two-step process—the first step to recover the monoprotic acid and the second step after distillation to reject the water from the diffusion process—about 55 percent of the bright dip was recovered. Because of problems mixing the solution back into the appropriate concentrations, more work is needed to perfect this type of recovery.

Diffusion dialysis is a very cost-effective way of recovering spent acid waste streams. Looking at the cost-based analysis (Table 1) brings up the following examples: The cost of the original bath, the hydroxide used to neutralize the acid and precipitate the metal, the disposal of the sludge, and the cost to purchase the new acid for the next bath. It does not include the cost of the labor, polymer, clarifier, settling tank, and sludge dryer.

The cost of the recycled acid is shown in the bottom half of the table. It also includes the cost of the original bath, but the cost of the new solution and disposal of the waste equal only about 10 percent that of the treatment process. It does not include the cost of the recycling equipment, but this cost is much less than a treatment system and does not require as much labor. It also does not include the resale value of any reclaimed metal; however, that is offset by the cost of electricity to win it back from the liquid.

Recovery parameters are dependent upon acid concentration, TDS, DI water quality, and membrane exposure times. Membrane exposure was optimized for maximum metal rejection. These results are specific to the waste streams tested. Specific recovery will differ from these results because of differences in processing conditions.

Alkaline Cleaner Recycling Via Microfiltration

Alkaline cleaners and detergents are used in the metal finishing industry to remove oils and soils from the parts to be finished. They have been used for many years, but have been more and more in demand because of the regulations surrounding solvent use for degreasing. The problems associated with detergent cleaning are caused by the fact that the oils and dirt become suspended in the solution and inhibit cleaning power when they become too high.

Prior treatment methods have been to skim any floating oils from the surface and add detergent and/or caustic to maintain some arbitrary value. This allowed maximum solution life, but still made for occasional batch dumps of the spent cleaner, which was often bled into the waste stream and treated or discharged into the sewer.

Ultrafiltration

Ultrafiltration offers a new method of reclaiming dirty cleaning solutions and minimizing the waste generated from them. The ultrafiltration membrane is an organic film that has been polymerized and formed into sheets. These sheets are then rolled onto a supporting frame and installed into some type of tube or housing. The spent solution is passed through the membrane filter where oils and soils are rejected and water and detergent pass through. An automatic cleaning system periodically cleans the surface of the membrane, maintaining solution flow and filtration quality.

With the system installed at LLNL, a controller monitors the pressure across the membrane and cleans itself automatically. The system can also be set to clean manually, or not at all. Our experience with the system has been brief, but the process has impressed us with its ease of operation and the quality of the separation. Below is a brief collection of the data gathered during its trial run at LLNL.

	Initial	*Final*
Concentration	65 gm/L	61 gm/L
Alkalinity	0.84 N	0.83 N
Suspended oils	3.5 gm/L	0.14 gm/L
Suspended solids	5 gm/L	0.04 gm/L

As can be seen from the results, the detergent and alkalinity were affected very little, while the oils and dirt were almost completely removed. The systems ran for a total of 32 hr on the tank, and may have run much less if the detergent had been removed from the tank and fed from a holding tank. As it was set up, the intake and the outlet were in the tank simultaneously. This provided only a slow dilution of the dirt and oil. Because the flow through the membrane started at 1.1 gpm and finished at 4 gpm, with an average flow of 1.7 gpm, the total volume of the tank would have passed through the membrane in about four hr; the advantages of the holding tank became clear.

Another benefit to this system is that it can recover synthetic cutting and cooling fluids from machine shop waste. By filtering out the oils from this waste, the fluid can be reused instead of discarded. This use is currently being evaluated at LLNL and further data will follow on its effectiveness.

Electroless Nickel Recycling Via Electrodialysis

Electroless nickel is a coating that has found wide use in the finishing industry. The ability to deposit evenly on a variety of surfaces and replicate or enhance the surface finish, the high hardness and corrosion resistance, and the machinability of the deposit have all been factors in its success. Two of its drawbacks are the limited solution life, and the tendency to spontaneously plate-out on the tank and associated equipment. These problems can contribute to a higher cost per unit plated. Electroless nickel solutions also require some type of waste treatment to dispose of its spent solution. This is typically done using precipitation techniques where a hydroxide sludge is generated.

The limit to bath life is inherent in the solutions chemistry. By using hypophosphite as the reducing agent for the nickel ion, the by-products are nickel metal and orthophosphite. When the level of orthophosphite in the solution reaches too high a concentration, the reaction slows and finally stops. The bath must be disposed of, and its replacement and treatment costs can be quite high. The tendency to plate-out can be influenced by dissolved solids in the bath, and can also cause a bath to have to be discarded.

The electrodialysis process uses a membrane, deionized water, and an electromotive potential to separate the orthophosphite, nickel ions, and dissolved solids. This allows the bath to be reused many times without disposal.

Testing

The first trials of the bath were performed on a solution that had been operated over a 40-day period. This bath had five metal turnovers, and its deposition rate had dropped from .0006 in./hr to < .0002 in./hr. The first step was to measure the dissolved solids content. In this case, the TDS was about 165,000 ppm. The nickel metal was still at 6.8 gm/L and the hypophosphite was at 40 gm/L.

After filling the holding cell with deionized water, the unit was plumbed to the tank and the recirculating pumps activated and adjusted to 4 gpm of plating solution through the recovery membrane, with 6 gpm of water through the rejection membrane. The DC power supply was adjusted to 15 amperes and 3 volts.

Table 2

Batch Operation, Precipitation, Disposal & New Solution Makeup

Nickel metal	20 vol% x $22.50/gal x 100 gal	=	$450.00
Hypophospite	3.3 vol% x $25/gal x 100 gal	=	82.50
Disposal	12 lb x $1.85/lb	=	22.50
New solution makeup			
Nickel metal	20 vol% x $22.50/gal x 100 gal	=	450.00
Hypophospite	3.3 vol% x $25/gal x 100 gal	=	82.50
	Total	=	**$1087.50**

Dialysis Recycling & Rejuvenation

Nickel metal	20 vol% x $22.50/gal x 100 gal	=	$450.00
Hypophospite	3.3 vol% x $25/gal x 100 gal	=	82.50
Rejuvenation			
Nickel metal	1 vol% x $22.50/gal x 100 gal	=	22.50
Hypophospite	1.5 vol% x $25/gal x 100 gal	=	37.50
	Total	=	**$592.50**
	Total Savings	=	**$495.00**

After 22 hr of operation, the voltage had increased to 12 volts and the liquid in the holding cell had turned slightly green. The TDS in the plating solution had decreased to 70,000 ppm. This is essentially what a new bath has to start with. After replenishing the hypophosphite in the plating bath and adjusting the nickel to the correct operating concentration, the bath was heated to 92 °C and a test panel was plated.

The plating rate had increased to almost .001 in./hr. This bath was then operated for another five metal turnovers and re-treated in the same fashion, with equally successful results. It has since operated for many metal turnovers and dialysis runs, and the only time there has been a problem is when the tank has plated out and must be stripped. There has been some talk of installing a small anodic DC current to the tank and heater to minimize the reduction activity, but this is still in the planning stage. It is theorized that this bath could run indefinitely with dialysis and replenishment.

At this point, a low-phosphorous bath was chosen for recovery investigation. Its initial plating rate was .001 in/hr. This bath had been used for plating on aluminum and had plated out on the heater and tank walls several times during its operation. This was probably caused by the dissolved zinc that resulted from zincating prior to plating. This bath had an initial TDS of 225,000 ppm. It was hooked up the same way and operated for 26 hr until the TDS had been reduced to 80,000 ppm. The hypophosphite and nickel were replenished, and the bath was heated to 90 °C. The plating rate from the recovered bath was a little less than .001 in/hr. The bath was very stable and operated for two turnovers before it started to plate-out on the heater. The tank and heater were stripped and the solution continued to operate until the TDS increased to 200,000 ppm. At this point, the bath is being saved and awaiting reuse when the low-phosphorus deposit is again requested.

Several other chemistries were tested with similar results. Only one chemistry presented any problem. With this bath, the plating rate increased to .0016 in./hr after processing through the dialysis process. The solution became unstable, and then plated-out on the tank walls and heater. No matter what was done chemically, the bath continued to do this. It was hypothesized that the stabilizer had been removed from the bath during dialysis. The manufacturer was called and declined to sell the stabilizer separate from the nickel concentrate. This chemistry may not be possible to recover with electrodialysis.

Cost savings for the operation can be quite high, depending on the cost of the treatment chemical and disposal costs. A sample cost savings estimate is included in Table 2 for comparision. The data show that the $12,000 cost of the electrodialysis equipment is quickly recovered by the reduction in chemicals purchased and associated waste treatment costs. The operation is simple and runs unattended, except for maintaining liquid levels and monitoring the TDS. The process has been used on several different types of electroless nickel baths and only one has proven to be unsuccessful.

Summary

The collaborative effort between LLNL and NCAMF has been successful in a number of areas:

- Familiarizing metal finishers in the Northern California area with facilities at LLNL
- Providing the chance for these small businesses to visit and/or call LLNL for consultation and technical assistance
- Providing an opportunity for LLNL metal finishers to evaluate low-cost recycling options for processes such as acids, electroless nickels, and cleaners, and to offer these options to the industry

The demonstrated success of the program has resulted in the Small Business Office at LLNL recently approving another year of sponsorship of this program. In this phase, LLNL personnel will continue to work with NCAMF members, attempt to expand our efforts to non-members, and to start a collaboration with the Metal Finishers Association of Southern California (MFASC). **P&SF**

About the Author

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Steffani attended San Jose State University, specializing in materials engineering. He has been involved with the metal finishing industry since 1976, and has spent the last 10 years at LLNL. Prior to this, he was with Stanford University's Linear Accelerator Center. His interests include electroforming and waste minimization, and he has written more than 15 technical papers and articles for publication/presentation at symposiums through the country.

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Editor's Note: *In response to reviewer comments, Mr. Steffani emphasizes that this paper was written to showcase a program between LLNL and the NCAMF. While figures are based on laboratory data, not production runs, it is likely that a follow-up paper will report on results gained from industrial use in production facilities within the NCAMF. In his comments to the editorial staff, Mr. Steffani noted that LLNL finishes more than 20,000 items per year, and the waste streams processed are actual, not synthetic. The dollar figures cited in the tables are what LLNL pays to dispose of waste—these numbers would likely change for larger or smaller users. Chemical treatment may be more economical now than equipment-based technologies, but is not a conscientious environmental option for the long-term.*