Optimizing Anodizing Baths with Diffusion Dialysis

by Daniel E. Bailey,

Diffusion dialysis is ideally suited for the recycling of sulfuric acid anodize solutions. Diffusion dialysis provides improved anodize quality, consistent anodic thicknesses, cooler and less energy-demanding baths, while eliminating production downtime associated with the dumping and remaking of the anodize bath. The passive, continuous diffusion dialysis process enables the anodizer to efficiently remove and control the dissolved aluminum content in the bath while recovering and returning a high percentage of the sulfuric acid back into the process bath. The diffusion dialysis process also removes and controls other contaminant build-up in the anodize bath, such as copper, iron, lead, magnesium, manganese, silicon, and zinc, while producing a minimum of rejected waste byproduct for subsequent treatment and disposal.

This article reviews diffusion dialysis technology and relates its benefits to anodizers.

WHAT IS DIFFUSION DIALYSIS?

Diffusion dialysis is a membrane separation process. It has been successfully used for many years for the separation and recovery of acids from dissolved metal-bearing solutions. Diffusion is the spontaneous movement of a material from an area of high concentration to an area of lower concentration. Driven by the concentration difference, the movement of material will continue on its own until the concentration difference no longer exists. Dialysis is the separation of molecules due to the differences in the rate of movement of the molecules through a semi-permeable barrier.

In the recovery of acids with diffusion dialysis an anion exchange membrane acts as a semi-permeable barrier placed between a flowing water stream and a flowing acid with dissolved metal solution. The anion exchange membrane has fixed positive charges located on its surface. These positive charge locations attract the negatively charged anions in solution that come in close contact with the anion exchange membrane surface.

In the case of sulfuric acid anodize baths the overwhelmingly predominant anion is the sulfate ion, SO_4 . As these sulfate ions in the sulfuric acid anodize solution are attracted to the membrane they are also driven by the concentration difference to diffuse across the membrane to the water side. Simultaneously, the thermodynamic Law of Electroneutrality (in solution total charge must balance to zero) requires that the transference of every sulfate ion, which carries two negative charges, be accompanied by the transference of two positive charges. Positively charged ions, such as Al^{+3} or other metal ions, are strongly inhibited from crossing the positively charged membrane because of the repulsion between like charges. The hydrogen ion, present in the acid solution as H_3O^{+1} ions, or protonated water, is also positively charged, but is able to cross the membrane with very little hindrance. This is due, in part, to the high concentration of hydrogen ion in the acid solution and also, in part, because of the highly associated nature of water, which allows the hydrogen ion to effectively delocalize its charge. The net effect is that the rate of diffusion of sulfuric acid across the membrane is an order of magnitude greater than that of the dissolved aluminum. Finally, by causing the flow of the acid solution to be in the opposite direction to the flow of water (counter-current flow), optimal advantage of the necessary concentration gradients can be realized. The results are that the water entering the diffusion dialysis system exists as a metal-depleted recovered acid solution and that the acid solution entering the diffusion dialysis system exists as an acid-depleted dissolved metal-bearing solution.

APPLIED DIFFUSION DIALYSIS

The standard processing rate for diffusion dialysis systems is a liter per hour per square meter (approximately 0.025 gal/hr/ft²) of available anion exchange membrane surface area. To obtain the necessary membrane area that is required to process large volumes, the membranes are stacked between gasketed hydraulic flow spacers. These membrane stacks are usually standardized over a range of differing processing capacities.

Figure 1 depicts a typical, automatically operated acid-recycling configuration. The acid-recycling system has two liquid chambers at the top of the unit: one chamber is for water and the other is for the acid to be processed. A dual set of level controls is located in each chamber. As the acid level drops in the chamber the primary level controller will energize a pump located on the base of the system. Acid solution will be drawn into this pump and then sent through a filter and into the acid-holding chamber on top of the module.

Once the acid-holding chamber has been refilled the primary level controller will shut off the pump. Should the primary level controller fail for some reason a secondary level controller will shut off power to the system at emergency-high or emergency-low level and an audible alarm will sound.

A similar dual arrangement is present in the water-holding chamber. Instead of a pump the primary level controller is tied into a solenoid valve,

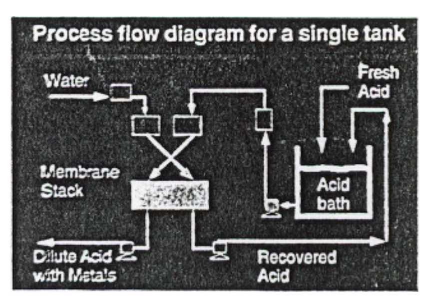

Figure 1. Acid-recycling flow schematic.

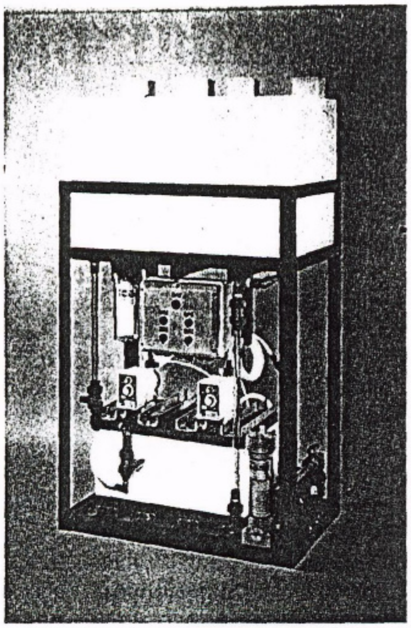

Figure 2. Typical diffusion dialysis acid-recycling system.

which is plumbed to the water feed line.

Once the water and acid solutions are in the holding chambers on the unit they flow independently by gravity into the membrane stack on the base of the unit (see Fig. 2). The acid and water solutions flow counter-currently through the membrane stack, thus maximizing usage of the concentration gradients. Using the principles of diffusion dialysis, anion exchange membranes segregate acid molecules into a purified zone. Typically, 80 to 95% of the acid is recovered with 80 to 95% of the metals removed.

The exit ports of the membrane stack are plumbed to a set of metering pumps. Except during the automatic refilling of the system these metering pumps are the only moving components on the entire system. The metering pumps are used to control the solution flow rates. The exit ports of these metering pumps are plumbed either back into the acid process tank, for the recovered acid stream, or in the case of the metal-rich, acid-depleted waste, plumbed to final treatment.

The acid-recycling system is a fully modularized unit. For installation the pump on the acid-recycling unit is plumbed to the working anodize tank(s) and a solenoid valve on the unit is plumbed to a pressurized water source. The system uses 115 V AC/20 Amp service and upon delivery can be plugged in and immediately utilized.

IMPLEMENTING ACID RECYCLING

In 1995 three 10 gpd diffusion dialysis systems were installed onto three 1,000-gal sulfuric acid anodize tanks at an anodizing job shop located in Santa Clara, Calif., for control of aluminum and contaminant build-up and recovery of sulfuric acid. Quality control through consistent anodize bath purity was a major motivating force in the implementation of these units.

To prove its effectiveness in removing metallic contaminants and in producing workable concentrations of acid, pilot studies were performed on the anodizing solutions. The pilot studies showed excellent results in removing metallic contaminants as well as generating a recovered acid permeate of sufficient concentration for reuse. The acid-depleted fraction following dialysis produced a solution, which was rich in metal and weak in acid concentration.

The sizing of the diffusion dialysis system was based upon the volume of spent anodizing solution that was previously produced, the rate of this production, and the efficiency of the diffusion dialysis process. A useful "rule of thumb" requires that, at a minimum, the volume of spent acid that was previously discarded be recycled once through the diffusion dialysis unit over the same period of time that it took to generate the spent acid.

The three 10-gpd acid-recycling systems were installed directly onto the anodizing process tanks. Additions of virgin acid are made to replenish depleted volumes due to consumption, dragout, exhaust escape, and (he minor amounts lost in the dialysis process.

Table I is representative of the diffusion dialysis performance results of this installation. Recycling efficiencies were calculated by comparing the recycled acid concentrations to the initial anodize bath concentrations.

In 1995 an anodizing job shop located in Pawtuckct, R.I., installed a 20-gpd diffusion dialysis system onto a 1,000-gal sulfuric acid anodize tank for control of aluminum and improved quality control. In 1996 another 20-gpd diffusion dialysis system was installed onto a 1,000-gal sulfuric acid hardcoat tank that contained glycerin as an additive. It was found that about two-thirds of the glycerin was also recovered with the reclaimed sulfuric acid. These anodizing baths have not been dumped since.

COMPARISON OF DIFFUSION DIALYSIS TO RESIN SORPTION TECHNOLOGY

Resin sorption technologies have often been successfully utilized for the recycling of aluminum anodizing baths. This technology relies on the sorption of acid molecules on an ion exchange resin bed. The process works by pumping contaminated acid into the bottom of the resin bed. Acid is sorbed by the resin particles and the partially deacidified salt solution is collected from the top of the bed. Water is then pumped into the top of the bed, desorbing the acid from the resin and the recovered acid product is collected from the bottom of the bed. The above cycle is continuously repeated by alternately opening and closing a series of valves.

Acid recovery efficiency via resin sorption can vary from 70 to 95% per

Table I. Anodize Recycling Performance

	Anodize Acid	*Recycled Acid*	*Depleted Acid with Metal*
H_2SO<. g/L	188	170	39
Aluminum, ppm	6,600	<100	6,300
Copper, ppm	83	5.4	127
Iron, ppm	123	8.7	118
Magnesium.ppm	205	1.3	220
Zinc, ppm	280	13	310
Acid-recycling efficiency:		90.4%	
Aluminum elimination efficiency:		95.4%	
Copper elimination efficiency:		93.5%	
Iron elimination efficiency:		93.0%	
Magnesium elimination efficiency:		99.3%	
Zinc elimination efficiency:		95.4%	

pass; however, metal removal rates per pass can be as low as 25%. One reason for this low aluminum removal efficiency is due to the entrapment of process solution that is still contaminated with aluminum in the resin bed column. This entrapment hinders overall recycling efficiency because it requires multiple passes to achieve sufficient metal removal. For example if a bath is maintained at 6 g/L aluminum and the bath normally builds up to a tolerable limit of 12 g/L in 10 days then the system must remove a mass of aluminum equivalent to 6 g/L times the entire volume of the bath in the same 10 days. If the system has an aluminum removal efficiency of 25% per pass it must process the entire volume of the bath 4 times in 10 days. Assuming that 90% of the acid is recovered in each pass and that the acid concentration in the bath is maintained at 15% by weight, 1.5% by weight of the acid is lost in each pass. After 4 passes a total of 6% by weight of the acid is lost.

By contrast, diffusion dialysis systems will typically remove 90% or greater of the aluminum per single pass while recovering 90% of the acid. In the hypothetical case described above -a diffusion dialysis system will require 1.1 passes (6 g/L H- [0.9 X 6 g/L]) to remove 6 g/L of aluminum. After 1.1 passes at 90% acid recovery a total of 1.7% by weight of acid will be lost. The effective net efficiency of acid recovery is, therefore, only 89%. Thus, significantly less waste by-product is produced, typically one-half to one-fifth as much. When assessing the benefits of any recycling technology it is important to closely look at the volume and content of the waste by-products produced and balance this with the volume and content of the products recovered.

With the advent of significantly more durable ion exchange membranes in recent years, the life expectancy of the ion exchange membranes utilized in sulfuric acid recovery is between 10 to 20 years. Typical ion exchange resin life in acid sorption systems varies between 2 to 10 years. Both technologies require very good prefiltration of the process solution prior to introduction into the recovery units.

JUSTIFICATION AND BENEFITS

At anodizing job shops and captive shops across the U.S. diffusion dialysis users report improved anodize quality and reduced rework, often with reduced processing times. Additionally, dialyzed anodize baths tend to run cooler, using less energy, and thus cost less to operate. The following is a summary of benefits being derived from the implementation of acid recycling utilizing diffusion dialysis:

- Savings from reduced or eliminated disposal costs and reduced acid purchases
- Elimination of production downtime associated with the dumping and recharging of acid baths
- Minimization of direct operator contact with dangerous chemicals—reduced operator exposure
- Fully automatic operation, 24 hours per day, 7 days per week, with very minimal operating costs
- Improved process control with consistent anodic thicknesses improves quality and minimizes waste

SUMMARY

Diffusion dialysis for acid recycling has many benefits. It reduces acid purchases and eliminates or lowers neutralization or hazardous waste hauling costs and the related liability. Toxic chemical use is reduced and the required reporting and handling of hazardous materials and associated labor is greatly reduced. Consistent bath strength yields greater product uniformity and better quality with lower operating costs. Diffusion dialysis can dramatically improve a facility's quality and economic performance.

Biography

Daniel E. Bailey is Manager of Industrial Chemical Purification Resources of Palmer, Ma. He has a BS degree in Chemistry from Northeastern University and an MS degree in Applied Management from Lesley College. He has over 17 years of experience in membrane technology and has two patents for acid recycling with diffusion dialysis. MF