

RECYCLING OF NITRIC-HYDROFLUORIC ACID WITH DIFFUSION DIALYSIS

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Stainless steels can be pickled in a variety of acid solutions to remove scale and to eliminate weld and machining marks, in order to blend the final finish into the original mill finish. A common choice among stainless steel fabricators is a mixture of Nitric and Hydrofluoric acid. Varying formulations of this chemistry are used to adjust etch rates and temperature requirements, dependent upon the type and condition of the stainless steel parts that are being pickled.

As the stainless steel is pickled, metallic components of the alloy are oxidized from the surface of the part into the acid pickling solution, producing metal salts in solution, and liberating hydrogen gas in the reduction reaction. As the concentration of metal salts increase in the pickling solution, the rate of oxidation of the metallic substrate will be affected. Although a small amount of metal salts dissolved in the pickling solution will initially enhance the dissolution rate of metal oxides at the surface of the part, -catalyzing the electron transfer step from the metal to the hydrogen ion at the solution-substrate interface, - generally the rate of pickling will decrease as the metal salt concentration in the pickling solution increases. At some point, dependent upon the operational parameters of the particular pickling bath, the pickling rate will become unacceptably slow or incomplete, decreasing both the quality and the throughput of the pickling operation. At this point, the pickling bath is either discarded and made up with a fresh acid mixture, or partially discarded and refreshed with the appropriate acid mixture. The spent pickling acid is either treated in-house or contracted for disposal off-site. Hauling away spent pickling acid is typically an expensive proposition, which requires a significant amount of paperwork. Disposal also subjects a company to long-term liability for its hazardous waste by-product. Treating the spent acid in-house requires added capital investment, labor and operational cost, and exposes plant personnel to increased health and safety risks.

Diffusion Dialysis is ideally suited for the recycling of Nitric-Hydrofluoric acid, stainless steel pickling solutions. Diffusion dialysis provides improved pickling quality, consistent pickling rates, and less energy demanding pickling baths. It also eliminates production down-time associated with the dumping and remaking of the pickling bath. The passive, continuous Diffusion Dialysis process enables the stainless steel pickler to efficiently remove and control the dissolved metal content in the bath while recovering and returning a high percentage of the acid mixture back into the process bath. The Diffusion Dialysis process also removes and controls other contaminant build-up in the bath, while producing a minimum of rejected waste by-product for subsequent treatment and disposal.

This paper reviews Diffusion Dialysis technology and relates its benefits for the recycling of Nitric-Hydrofluoric acid solution used for the pickling of stainless steel.

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 solution with dissolved metal. 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 nitric-hydrofluoric acid pickling solution, the overwhelmingly predominant anions are the nitrate ion, NO_3^{-1} and the fluoride ion, F^{-1} . As these nitrate and fluoride anions in the acid solution come in contact and are attracted to the positively charged membrane, they diffuse across the membrane into the less concentrated water solution on the other side of the membrane. This is due to the concentration difference across the membrane. Simultaneously, the thermodynamic Law of Electroneutrality (in solution total charge must balance to zero) requires that the transference of every nitrate or fluoride anion across the membrane be accompanied by the transference of a positive charge. Positively charged ions such as the ferrous cation, Fe^{+2} , or the nickel cation, Ni^{+2} or other metal cations, 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^+ ions, or protonated water, is also positively charged, but is able to cross the membrane with very little hindrance. This occurs for two reasons: the highly associated nature of water allows the hydrogen ion to effectively delocalize its charge, and because of the high concentration of hydrogen ions in the acid solution.

Diffusion Dialysis Separation Process

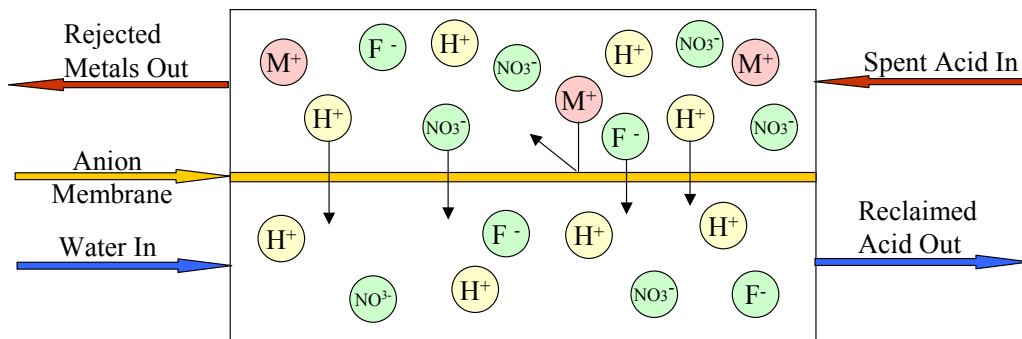


Figure #1

The net effect is that the rate of diffusion of nitric or hydrofluoric acid across the membrane is an order of magnitude greater than that of the dissolved metal cations. 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 exits as a metal-depleted recovered acid solution (diffusate) and that the acid solution entering the Diffusion Dialysis system exits as an acid-depleted dissolved metal-bearing solution (dialysate). See figure #1.

Applied Diffusion Dialysis.

The standard processing rate for Diffusion Dialysis systems is: a liter per hour per square meter (approximately 0.025 gallons/hour/square foot) 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.

Diffusion Dialysis Acid Recovery

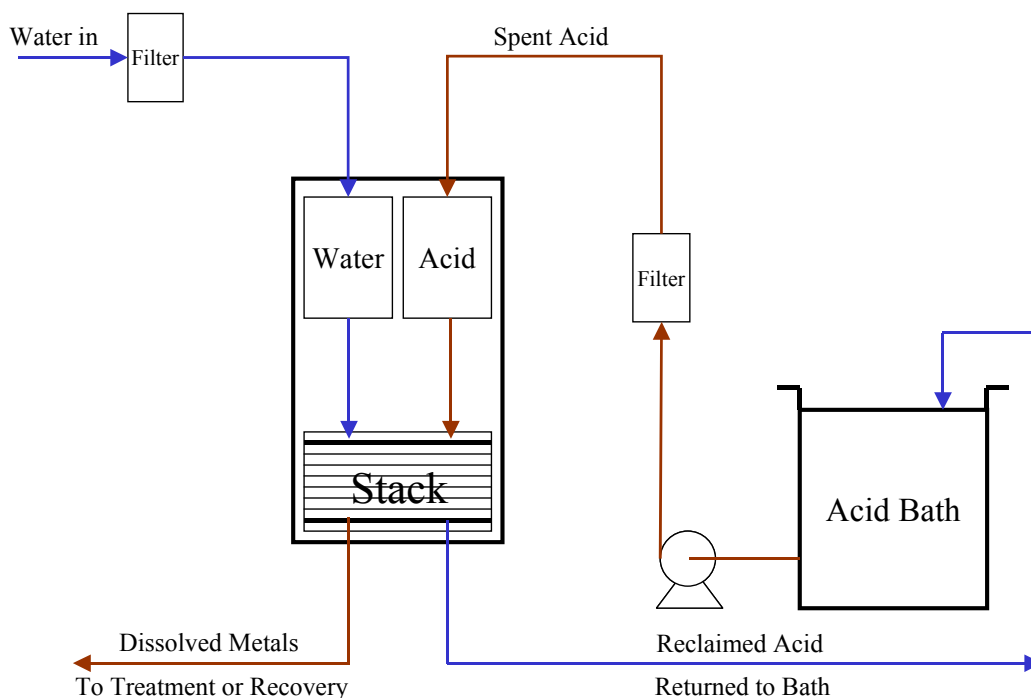


Figure #2.

Figure #2 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 self-priming air diaphragm pump located on 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 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(s) on the base of the unit (see Figure #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, 80-95% of the acid is recovered with 70-95% 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 the recovered acid metering pump(s) are plumbed into the acid pickling tank, and in the case of the metal-rich, acid-depleted waste solution, the metering pump(s) are 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 pickling tank(s) and a solenoid valve on the unit is plumbed to a pressurized water source. The system uses 115 VAC/ 20 AMP service and, upon delivery, can be plugged in and immediately utilized.

Implementing Acid Recycling -

A stainless steel pipe manufacturer began to investigate Diffusion Dialysis for the recovery of their Nitric-Hydrofluoric acid pickling solution and for control of metal and contaminant build-up in their pickling bath. Immediate motivation was for the replacement of a resin-sorption recovery system that had been marginally successful at recovering their pickling acid and controlling the metals in their bath. Adverse maintenance and reliability issues associated with the resin-sorption recovery system were key motivators for investigating alternative technologies.

Resin Sorption technologies have occasionally been utilized for the recycling of stainless steel pickling 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 de-acidified 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 between 40% to 90% per pass. Metal removal rates per pass can be as low as 25%. One reason for this low metal removal efficiency is due to the entrapment of process solution in the resin bed column. This entrapment hinders overall recycling efficiency because it requires multiple passes to achieve sufficient metal

removal. With Diffusion Dialysis technology, significantly less waste by-product is produced—typically one-half to one-fifth as much as with resin sorption systems.

With the advent of significantly more durable ion exchange membranes in recent years, the life expectancy of the majority of the ion exchange membranes utilized in Diffusion Dialysis acid recovery can be up to 10-20 years, dependent upon the application. Typical ion exchange resin life in acid sorption systems varies between 2-5 years. Both technologies require very good pre-filtration of the process solution prior to introduction into the recovery units.

To prove the effectiveness of the Diffusion Dialysis technology in removing metallic contaminants and in producing workable concentrations of recovered acid, a pilot study was performed at the customer's facility, by in-plant personnel, on their working pickling solution. The pilot studies showed excellent results in removing metallic contaminants and generated a recovered acid permeate of high 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 pickling solution 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.

A 600 GPD acid recycling system was installed directly on to the working pickling tank, as illustrated in Figure #1. Additions of virgin acid are made to replenish depleted volumes due to: consumption, drag-out, exhaust escape, and the minor amounts lost in the dialysis process.

Table #1 relates the Diffusion Dialysis performance results of this installation. Sixteen sample sets were taken over a three month period and averaged. Recycling efficiencies (in parentheses) were calculated by comparing the recycled acid and rejected metal concentrations to the initial pickling bath concentrations. The system is dialyzing about 500-600 gallons per day. A flow imbalance between the reclaim stream and reject stream can produce concentration increases, as seen in the increased nitric acid concentration in the reclaimed acid solution as compared to the initial nitric acid concentration.

<u>TABLE #1</u>	<u>INITIAL ACID</u>	<u>RECLAIMED ACID</u>	<u>REJECTED METAL</u>
NITRIC ACID	10.0%	11.4% (114%)	1.8% (18%)
HYDROFLUORIC ACID	2.5%	1.7% (68%)	0.8% (32%)
IRON	2.4%	<0.5% (<20%)	1.7% (71%)

For this stainless steel fabricator the major benefit was cost savings. Capital investment for a 600 GPD Diffusion Dialysis acid recycling system is \$144,500. After start-up of the system at this facility, monthly savings from reduced chemical purchases and elimination of off-site disposal are \$8,000 per month. With an operational cost of less than \$0.01 per gallon processed

(less than \$5.00 per day), payback for this system was reached in about a year and a half. There were also quality improvements and a decrease in production down-time. The environmental benefits are also significant with the elimination of hundreds of thousands of pounds of hazardous waste generation and the associated off-site disposal.

Justification and Benefits.

Cost savings are a major justification for using Diffusion Dialysis for the recycling of pickling acids. Diffusion Dialysis acid recycling users obtain improved quality and reduced rework, often with reduced processing times. 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 down-time 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, seven days per week, with very minimal operating costs.
- Improved process control with consistent pickling rates, improved quality and minimized waste.
- Improved environmental impact.

Summary.

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