Economic and chemical comparisons of hydrochloric acid recovery technologies for iron pickling operations

This paper evaluates available technologies to recover hydrochloric acid from spent wire pickling solutions. It includes a review of the operating and maintenance expenses and a case study that examines energy consumption, chemical mass balance and end products.

By Jared Cullivan and Bryan Cullivan

Metal fabrication and finishing operations involving ferrous metals require an intermediate process to remove oxides and other impurities from the surface of the metal. The most common intermediate process is acid pickling, and hydrochloric acid is the primary acid utilized worldwide to facilitate the process. Sulfuric, nitric, and phosphoric acids also perform the same task.

The resultant waste generated from hydrochloric acid pickling is an acidic ferrous chloride solution that is categorized as a hazardous waste product. The following is an economic and chemical comparison of the three leading technologies for reducing or eliminating waste hydrochloric acid, as listed in Table 1.

Chemical	Input (kg/hr)
HCl	12.5
$FeCl_2$	31.25
H_2O	164.25
Total	**208**

Table 1. Analysis of spent acid bath.

Acid Recovery (Sorption). This is a sorption process by which acid bonds to the resin inside an ion exchange column while allowing the ferrous chloride and water to pass through. The column is then backwashed with water to recover the absorbed acid on a batch basis.

Diffusion Dialysis (DD). This is a membrane process that operates under some of the same principles as Acid Retardation by utilizing ion selective membrane material. Clean water (dialysate) is introduced in counter-flow on the permeate side of the membrane to absorb the acid passing through the semi-permeable surface. DD is a continuous process.

Evaporative Recovery (ER). This utilizes co-flash vaporization and rectification to separate the ferrous chloride, hydrochloric acid, and water from each other. In the rectification step the acid is concentrated and water passes through for condensation, collection, and reuse in the rinse tank. Azeotropic HCl (17–22%) is possible with this technology.

Concentrate (waste) Generated	Acid Sorption		Diffusion Dialysis		Evaporative Recovery	
	(kg/hr)	%	(kg/hr)	%	(kg/hr)	%
HCl	0.5	0.3%	1.1	0.5%	0.75	1.1%
$FeCl_2$	13.95	4%	23.75	5.8%	31.25	40.8%
H_2O	172.75	95.7%	193.4	94.7%	44.5	58.1%
Total (kg/hr)	**187.2**		**218.25**		**76.5**	
Return Acid	**Acid Sorption**		**Diffusion Dialysis**		**Evaporative Recovery**	
	(kg/hr)	%	(kg/hr)	%	(kg/hr)	%
HCl	12	8%	11.4	6.2%	11.25	17.5%
$FeCl_2$	17.3	6.9%	7.5	2.2%	0	
H_2O	104	84.1%	164.85	91.6%	52.75	82.5%
Total (kg/hr)	**133.3 @ 8%**		**183.75 @ 6%**		**64 @ 17%**	

Table 2. Mass balance.

The scope of the following analysis is limited to waste hydrochloric acid from typical batch/continuous pickling. This paper does not discuss other chemical configurations or concentrations, nor does it discuss alternative configurations of the three stated separation technologies. Total cost estimates are based on primary contributing factors to capital, operating, and maintenance expenses.

What's noteworthy in this paper

WJI: Which technology best fits the wire industry?

J&B Cullivan: Evaluation of recovery technologies should be based on capital cost, waste or co-product handling, impact on production, and return on investment. Evaporation has several advantages over the alternatives, but the Acid Sorption producer has added better filtration and automated chemical analyzers to address some problem points. The evaporator's recovered acid is near the azeotrope (18%) and free of impurities, giving production people a consistent source of quality replacement acid. However, steam is required for the evaporation process.

WJI: Are there other recovery methods than those discussed here?

J&B Cullivan: Yes, pyrohydrolysis is commonly used to regenerate HCl on a very large scale. Due to the large capital and operating expense, pyrohydrolysis was not covered in this paper. Another hybrid technology based on evaporation is under development, but commercialization is still a few years away.

WJI: Do you find some people reluctant to make improvements because of the fear of the unknown?

J&B Cullivan: As more steel pickling plants successfully install and operate acid recovery, the fear factor subsides. All of the recovery methods addressed have overcome many of their initial weak points over the iterations of the products. Sorption systems have added better filtration equipment and online analytics. The evaporative process now operates at a lower temperature and has a smaller footprint. Sulfuric acid recovery evolved over the last three decades, and we see a similar trend with hydrochloric acid recovery technologies. Today, very few sulfuric acid pickle houses run without acid recovery. We expect the future of HCl and also mixed acids will follow that trend.

Jared and Bryan Cullivan

Questions for the authors? They can be contact at sales@betacontrol.com.

Data and chemical analysis

Analysis is based on a typical wire pickling operation with a spent acid bath as follows: five metric tons of spent pickle liquor per day (5,000 kg/day); 8% iron (by weight), 6% HCl (by weight).

Mass balance comparison of the three different technologies reveals advantages in the categories of acid recovery, metals rejection, concentrate reduction, and acid concentration.

Acid Sorption (Sorption) and Diffusion Dialysis (DD), unlike evaporative recovery, are not as energy intensive and have fewer components (Table 4). Literature on Sorption and DD reveals high percentage returns on the amount of hydrochloric acid returned (not regenerated) from the spent acid stream: 80-90% for Sorption (Cushnie[5], p. 246) and 80-95% for DD (Cushnie[5], p. 276). The mass balance on the spent pickle liquor showed acid recovery rates of 84.8% and 91.2%, respectively. Although the recovery rate of acid is high, the quality of the acid is low (8% and 6.2%, see Table 2). While DD has less than half the contamination of ferrous chloride in its return acid, the acid concentration is often too low to be returned directly to the pickle tank and requires additional concentration through evaporation due to the high volume (Cushnie[5], p. 278).

Sorption provides a better return acid in terms of concentration, 8%, but does not remove the ferrous chloride as effectively as the other technologies. Only 45.2% of the total ferrous chloride is rejected as concentrate/by-product.

Evaporative Recovery returns acid at a concentration near the azeotrope (in this case 17.5%) and reduces the concentrate/by-product mass by 63%, as compared with only 10% for Sorption and an actual 5% increase in mass for DD. In the absence of foreign contaminants that would affect the solubility (ex: zinc, chromium), ferrous chloride will begin to form a crystal when the iron concentration exceeds a saturation point in an evaporative recovery system. Crystallized ferrous chloride (tetrahydrate) is sometimes preferred as a co-product because of the lower

Utilities	Acid Sorption	Diffusion Dialysis	Evaporative Recovery
Electricity (kWh)	~4 (est.)	~4 (est.)	6.34
Water (L/hr)	112.2	194	~5 (est.)
Natural Gas (MMBtu/hr)	0	0	0.355

Table 3. Utility comparison for three methods.

Cost Analysis
Assuming the following rates:
• \$2.02 per MMBtu (U.S. Energy Information Administration, 2016)
• \$0.099 per kWh (U.S. Energy Information Administration, 2013)
• \$0.00073 per Liter H_2O (The Water Information Program, 2013)
• \$85.43 per metric ton HCl at 33% by weight (ICIS, 2006)
• \$70.00 per ton Lime (ICIS, 2006)
• \$0.26 per pound Wastewater Treatment Sludge (F006) (Cushnie[5], p. 361)
• \$0.10 per pound Spent Pickle Liquor Recycling (Cushnie[5], p. 362)
• \$1.18 per gallon HCl at 33% (ESTCP Cost and Performance Report: Spent Acid Recovery Using Diffusion Dialysis, 1999, p. 24)

Table 4. Cost considerations used for study.

shipping cost and higher resale value. An additional step is required to produce the ferrous chloride tetrahydrate.

Cost analysis and material costs

Table 3 shows cost factors for different expenses related to the process. The plant operation assumes the following for yearly calculations: 24 hour per day operation; five days per week (average); 50 weeks per year (average).

The specialized resin used to facilitate Acid Sorption (Sorption) is a primary material cost. Other common replacement materials include pump seals and filters. Sorption resin material has a life span of about five to 10 years for hydrochloric acid applications, Cushnie[5], p. 252. If insufficient filtration or extreme conditions occur, the life will be significantly shorter.

Membranes are the primary material cost for Diffusion Dialysis (DD). Other replacement materials include pump seals and filters. As in Sorption, pre-filtration is exceedingly important in DD compared to the thermal technologies because a scale or film will form on the inside of the membranes which will restrict acid diffusion and decrease the life of the membranes. DD membranes have a life span of about five years, Greiner[9], p. 18. Pre-filtration for acid retardation is critical and expensive as colloidal particles have a tendency to clog resin beds, blind the resins, and can create an uneven flow distribution that can affect performance.

Evaporative recovery systems do not have many regular material costs associated with their respective processes. Filters and pump seals are the only regular replacement items.

Process costs, uses and disposal

The education and technical ability is about the same for Acid Retardation (Sorption) and Diffusion Dialysis (DD) systems, requiring general knowledge of diffusivity and ion exchange, pipe fitting, and pump maintenance. Evaporative Recovery requires technical knowledge of operation and maintenance procedures for boilers and cooling towers, as well as pipe fitting and pump maintenance. Sorption, although a relatively simple operation in comparison to the other technologies, requires more frequent testing than DD and Evaporative Recovery (ER) and also requires more manual operations that will account for an increased labor cost.

Water and electricity are required for all three technologies. Water consumption is high for Sorption and DD but relatively low for evaporative recovery (cooling tower make-up water). ER has additional utility costs in the form of natural gas for the boiler.

All three technologies return over 90% of the free acid present in the spent acid. However, ER is the only technology that increases the concentration of the acid to any significant degree. The cost associated with the acid is the cost per year of additional acid required to replace the chlorides consumed either in the creation of the iron chloride salt or in the losses due to waste processing.

There needs to be a correction for the contamination of the return acid to the pickle tank. While all three technologies are designed for the same throughput, Sorption and DD actually require a larger throughput because the acid returning to the pickle tank is contaminated with ferrous chloride. Without a compensated cost associated with pickle tank contamination, the pickle tank concentration is unsustainable. Contamination correction includes the additional costs associated with the following: utilities, material, treatment, disposal and regulation.

All the technologies could require additional treatment of the resulting by-product. While the amount of caustic required in neutralizing the by-product is significantly reduced due to the acid recovery, it is not negated. Both the capital and operating cost of a conventional pH neutralization process should be considered in the capital cost considerations.

Utilities (\$/hr)	Offsite Disposal	Onsite Neutralization	Acid Sorption	Diffusion Dialysis	Evaporative Recovery
Electricity	0	0.2	0.396	0.396	0.628
Water	0	0	0.058	0.10	0.01
Natural Gas	0	0	0	0	.73
Total Cost	0	0.2	0.454	0.496	1.368

Table 5. Comparison of utility expenses for different methods.

The cost of disposal will vary greatly depending on the region and regulation. For the purposes of this paper, the following is assumed: neutralization performed onsite, sludge disposal by third party, and standard regulatory requirements for F006 waste. For a majority of ER operations, the concentrate by-product can be considered a co-product due to its high concentration and minimal acid content. There are a variety commercial uses for ferrous/ferric chloride in the water treatment industries and many ER operations have been able to offload the resulting concentrate at zero or negative cost. Assuming a client is found, the disposal cost for an ER operation is negated.

Regulation and issues related to ownership

An average cost of regulation for industrial wire plants in the United States is tabulated for the sewer. Acid Retardation (Sorption) and Diffusion Dialysis (DD) have sewer costs associated with neutralizing the concentrate. Evaporative Recovery (ER) disposal costs are based upon shipping the concentrate. Below is a discussion of issues related to ownership.

Sorption: In applications such as recovering hydrofluoric and nitric acid mixtures in stainless steel etching, this technology has flourished. The value of the acid (approximately four times HCl), cost of treatment and disposal, and the lack of competition justify the complexities of opera-

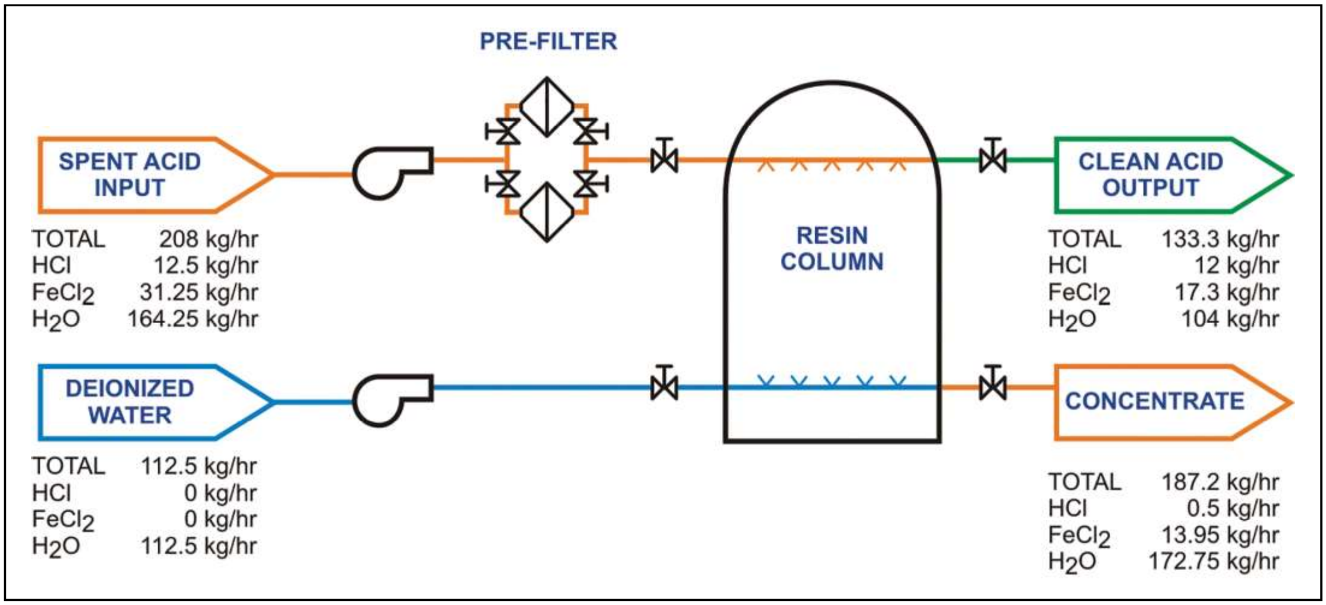

Fig. 1. Schematic of acid retardation (sorption) process.

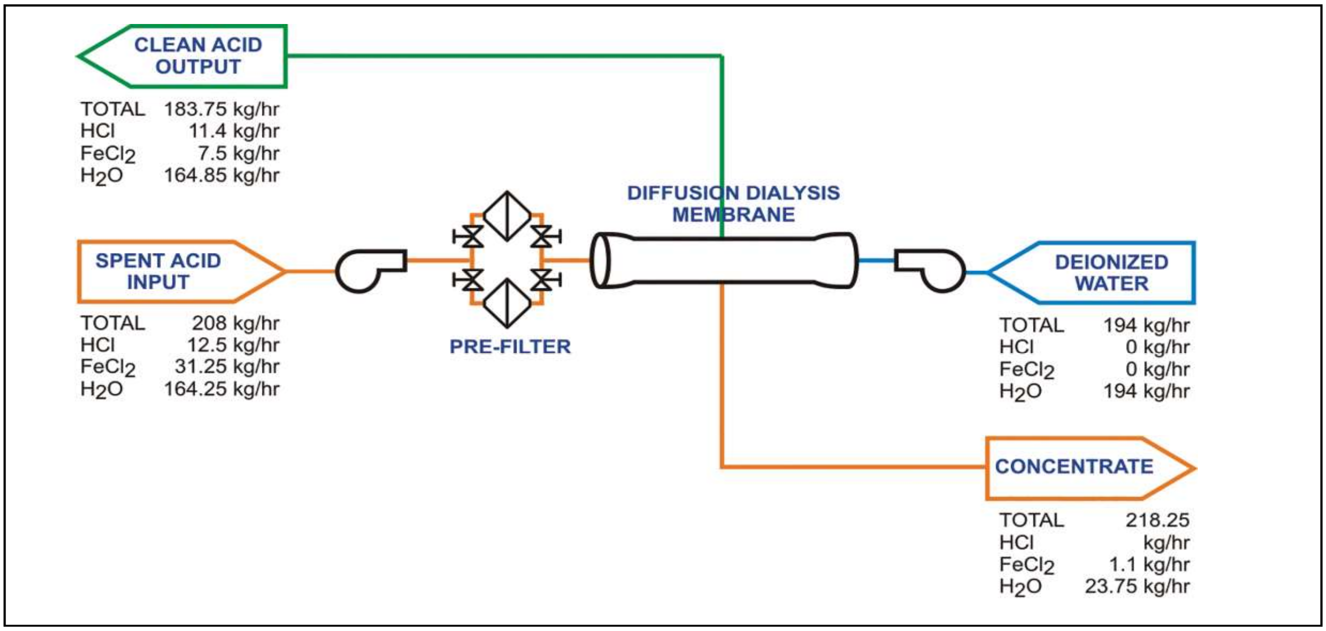

Fig. 2. Schematic of diffusion dialysis process.

Operating Cost ($/year)	Offsite Disposal	Onsite Neutralization	Acid Sorption	Diffusion Dialysis	Evaporative Recovery
Material*	0	82	3,980	35,023	822
Labor ($15/hr)	0	135,000	90,000	85,000	55,000
Utilities	0	1,200	2,724	2,976	6,544
Acid	146,400	146,400	88,800	91,680	92,400
Contamination Correction	0	0	44,527	55,396	0
Treatment	0	56,925	160	318	0
Disposal	278,437	182,711	50,895	88,151	46,080**
Regulation	27,300	21,558	22,673	25,384	5,841
Total Cost	452,137	543,876	303,759	383,928	206,687

* Includes resin, membranes, pump seals, and/or filters. ** Current shipping costs for disposal or reuse.

Table 5. Comparison of costs for different methods.

tion in the HF and mixed acid applications. Significant challenges of pre-filtration to extremely low levels to avoid resin fouling, resin shrinkage causing channeling and blow-through, and constant analysis to determine proper loading and regeneration are a few of the problems noted. The need to provide a complete waste treatment plant that generates sludge as the final by-product also brings into question the value of recovering a relatively cheap acid, Brown[3].

DD: This technology has not gained any traction in the steel industry. DD and electrodialysis have found applications in other industries, but the cost/benefit of the technology usually directs the steel industry to the other technologies.

ER: This method has been utilized in a variety of metals industries and the mining sector. The earlier "Atmospheric Evaporator" operated at around 115°C (240°F), necessitating the use of special plastics like PVDF to handle the corrosive, hot materials. The newer systems operate under a vacuum at approximately 80°C (175°F) and can use CPVC, polypropylene, and many FRP resins for components and storage. Although the systems are relatively small and simple to operate, they cost between US$6 and US$10 per metric ton of spent pickle liquor to operate. The value of the recovered acid is usually greater than the operating cost, but the issue of the remaining $FeCl_2$ concentrate still has to be addressed. There are many potential buyers/takers in North America who will use it for water treatment and flocculants, but in some cases the concentrate will have to either be treated with caustic and fed to a filter press or sent to a treatment facility.

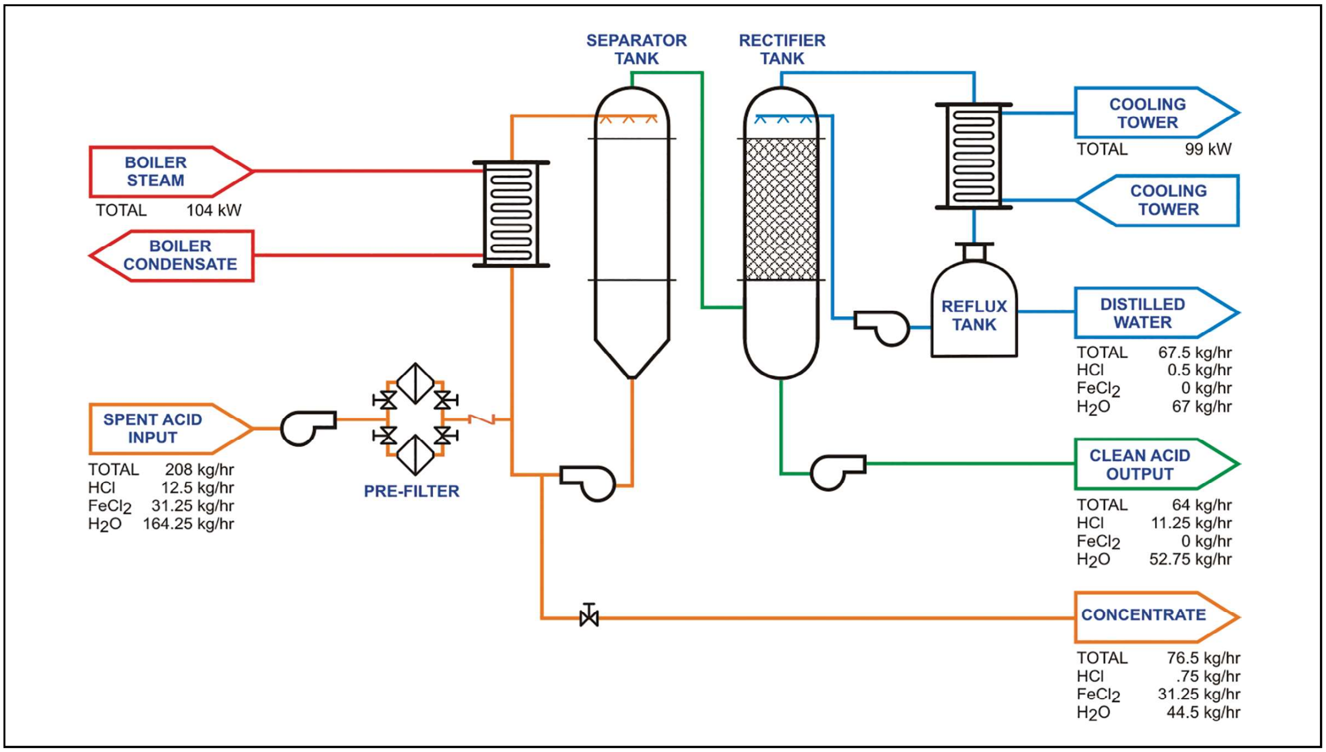

Fig. 3. Schematic of evaporative recovery process.

Summary

Sustainability. Environmental Stewardship. Green Technology. Joint and Several Liability. These words and phrases have taken seed and grown in the lexicon of the wire industry in this century. The wire industry must address the present and future impact of waste products, both economic and environmental. Since the creation of the EPA in 1970, the direction of legislation has been to reach Zero Liquid Discharge. Incorporation of resource recovery technologies provides a major step toward that "ZLD" goal. The disposal alternatives continue to contract in number and expand in cost, opening an avenue for competitive recovery technologies.

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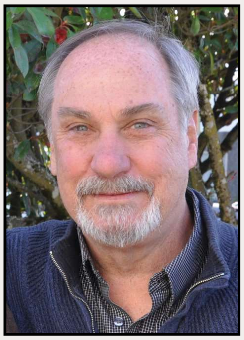
Jared Cullivan



Bryan Cullivan

Jared Cullivan is a process engineer and project manager at Beta Control Systems, Inc., in Beaverton, Oregon, USA, where for the last 12 years he has assisted with the design, automation, installation and commissioning of hydrochloric, sulfuric, and hydrofluoric acid recovery systems. He holds a B.S. degree in mechanical engineering from Santa Clara University. Bryan Cullivan is the founder (1980), president and CEO of Beta Control Systems, which has designed and installed over 120 environmental recovery facilities worldwide. He holds a B.S. degree in chemical engineering from Oregon State University. This presentation was made at Interwire 2015, Atlanta, Georgia, USA, May 2015.