

# Economic and Chemical Comparisons of Hydrochloric Acid Recovery Technologies for Iron Pickling Operations

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## Abstract

Evaluation of available technologies to recover hydrochloric acid from spent wire pickling solutions. Technologies reviewed include: pyrohydrolysis, acid retardation, diffusion dialysis, and evaporative recovery. A case study, based on typical batch/continuous pickling waste of hydrochloric acid operations, examines energy consumption, chemical mass balance, and end products. An economic review of the operating and maintenance expenses will be presented.

## 1.0 Introduction

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 four leading technologies for reducing or eliminating said waste product: Acid Retardation (Acid Sorption), Diffusion Dialysis, Pyrohydrolysis, and Evaporative Recovery (Evaporative Recovery).

- a) **Acid Retardation (Acid Sorption)** 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.
- b) **Diffusion Dialysis** is a membrane process that operates under some of the same principles as Acid Sorption (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. Diffusion Dialysis is a continuous process.
- c) **Pyrohydrolysis** is a roasting process in which the acidic ferrous chloride is burned to produce iron oxide and hydrogen chloride gas. The hydrogen chloride gas is then processed in an adsorption column where the hydrogen chloride gas reacts with

incoming water (usually rinse water from the pickling process) to form near-azeotropic hydrochloric acid.

- d) **Evaporative Recovery** 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 passed through for condensation and collection for reuse in the rinse. Azeotropic HCl (17 – 22%) is possible with this technology.

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 four stated separation technologies. Total cost estimates are based on primary contributing factors to capital, operating, and maintenance expenses.

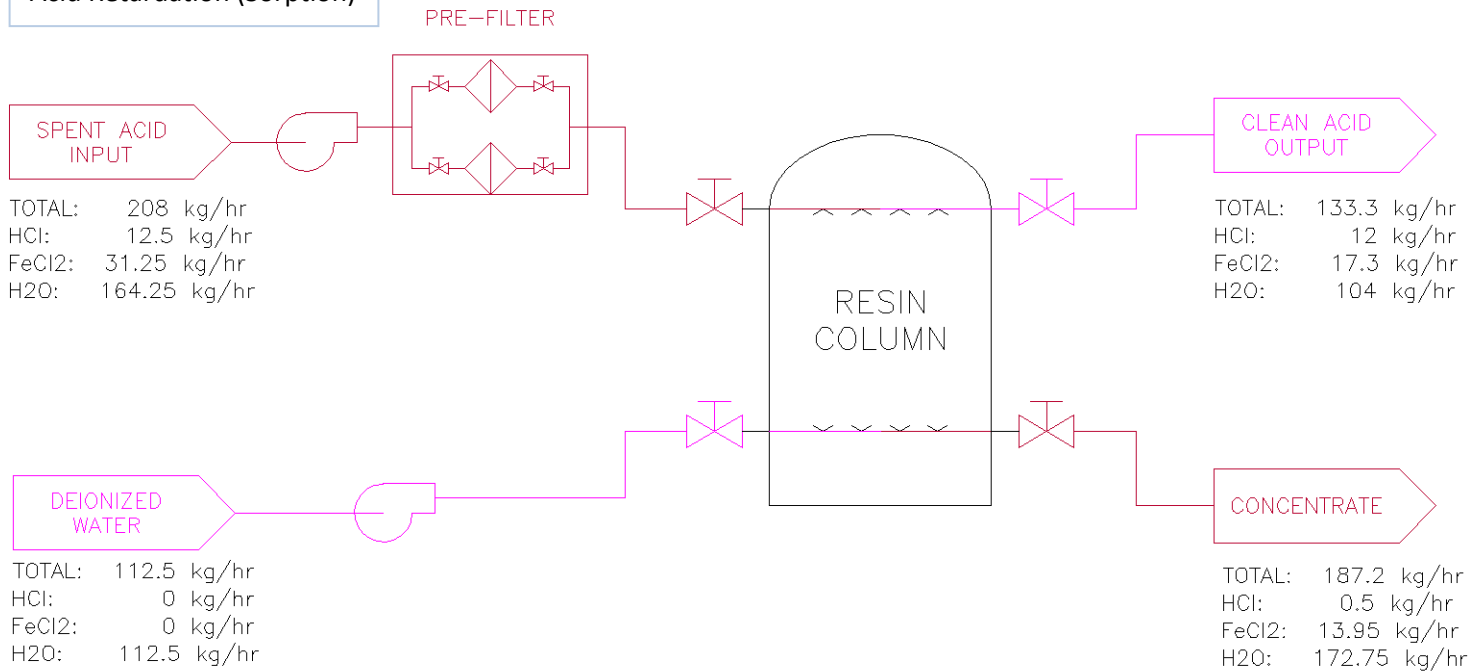
## 2.0 Data

Analysis is based on a typical wire pickling operation with a spent acid bath as follows:

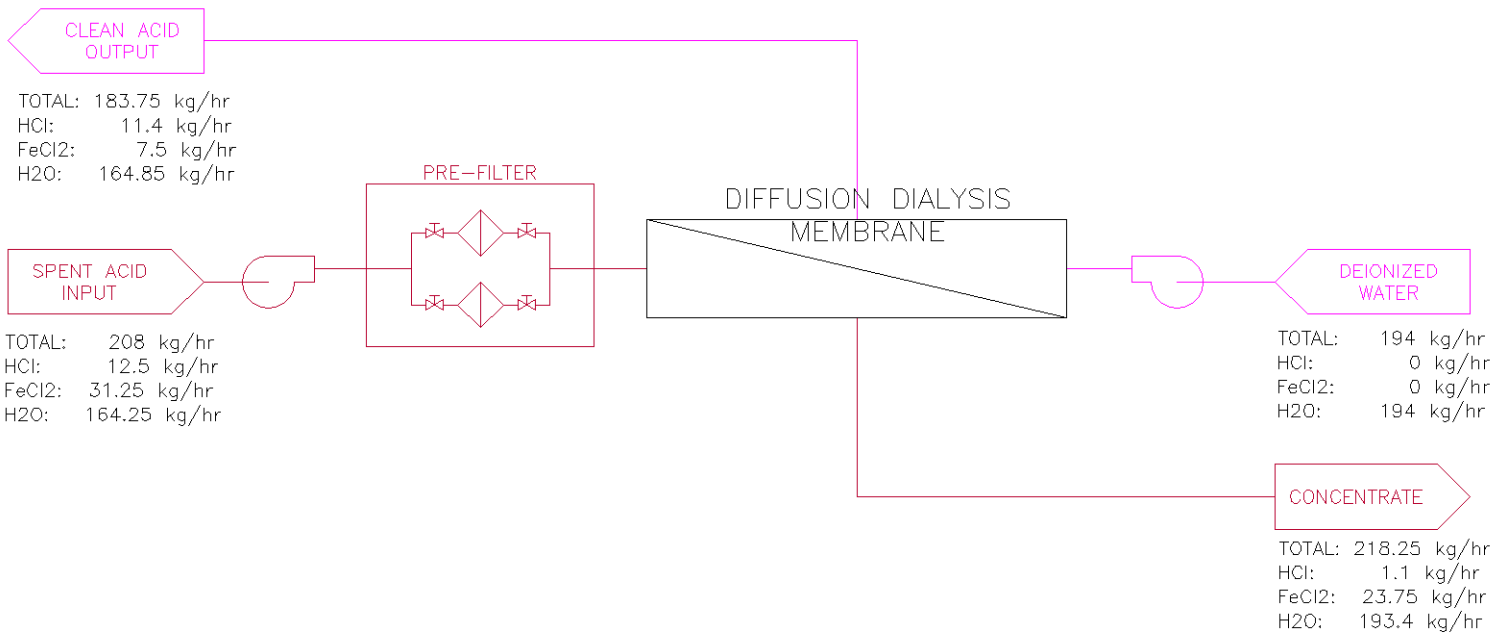
<b>INPUT: Spent Pickle Liquor</b> (5 metric tonnes/day = 208 kg/hr)		<b>(kg/hr)</b>
HCl	HCl 6% by wt	12.50
FeCl <sub>2</sub>	Fe 8% by wt	31.25
H <sub>2</sub> O		164.25
<b>Total</b>		<b>208.00</b>

<b>OUTPUT: Metal Concentrate Generated (Waste)</b>	<b>Acid Sorption</b>		<b>Diffusion Dialysis</b>		<b>Pyrohydrolysis</b>		<b>Evaporative Recovery</b>	
	(kg/hr)	%	(kg/hr)	%	(kg/hr)	%	(kg/hr)	%
HCl	0.5	0.3%	1.1	0.5%	N/A		0.75	1%
FeCl <sub>2</sub>	13.95	4%	23.75	5.8%	17.7 kg/hr (Fe <sub>2</sub> O <sub>3</sub> )		31.25	40.8%
H <sub>2</sub> O	172.75	95.7%	193.4	94.7%	N/A		44.5	59.1%
<b>Total (kg/hr)</b>	<b>187.2</b>		<b>218.25</b>		<b>17.7 (Fe<sub>2</sub>O<sub>3</sub>)</b>		<b>76.5</b>	
<b>OUTPUT: Return Acid</b>	<b>Acid Sorption</b>		<b>Diffusion Dialysis</b>		<b>Pyrohydrolysis</b>		<b>Evaporative Recovery</b>	
	(kg/hr)	%	(kg/hr)	%	(kg/hr)	%	(kg/hr)	%
HCl	12	8%	11.4	6.2%	30.25	17.9%	11.25	17.5%
FeCl <sub>2</sub>	17.3	6.9%	7.5	2.2%	1% (rinse reflux)		0	
H <sub>2</sub> O	104	84.1%	164.85	91.6%	139	82.1%	52.75	82.5%
<b>Total (kg/hr)</b>	<b>133.3 @ 8%</b>		<b>183.75 @ 6%</b>		<b>169.25 @ 17%</b>		<b>64 @ 17%</b>	

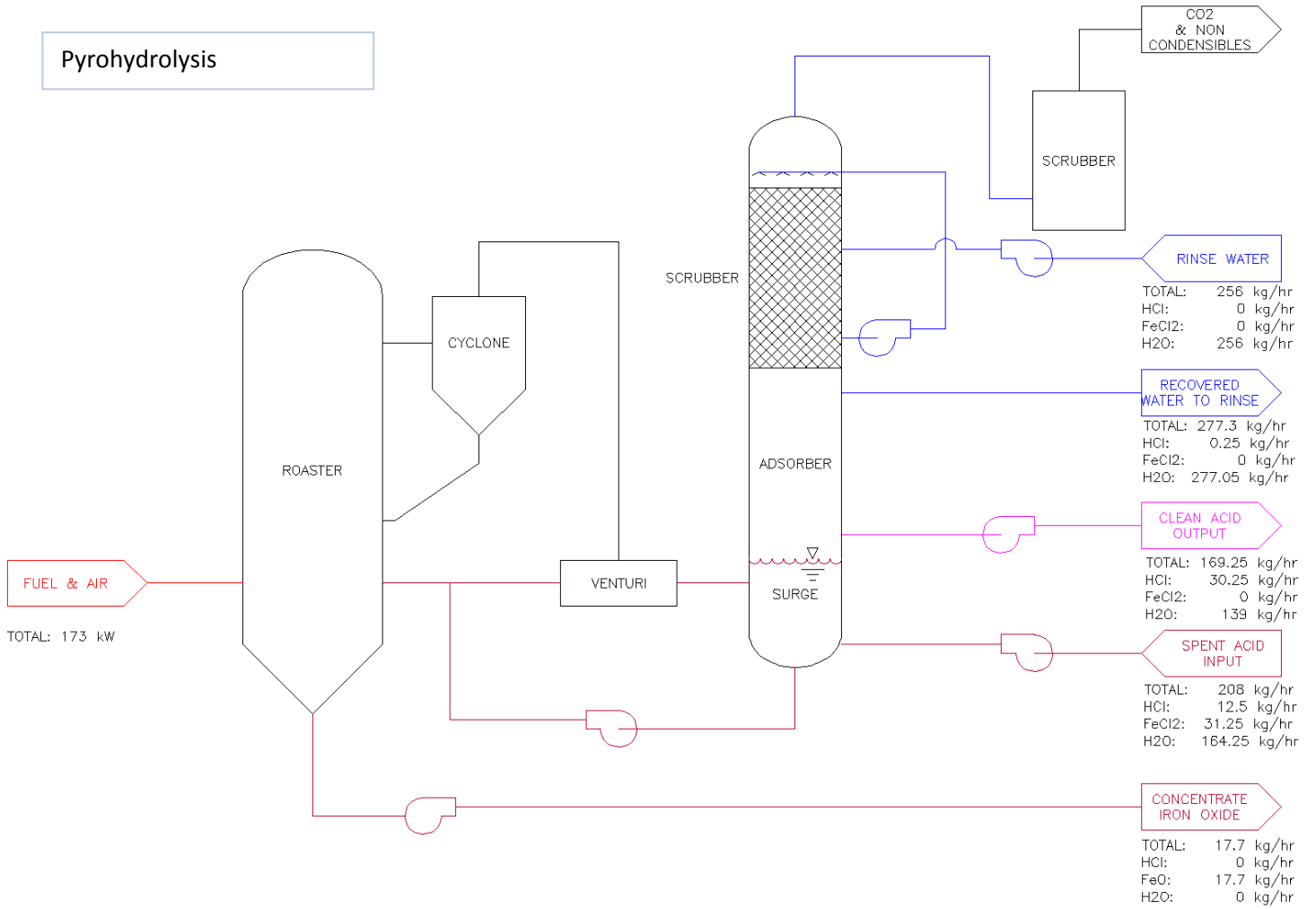
### Acid Retardation (Sorption)



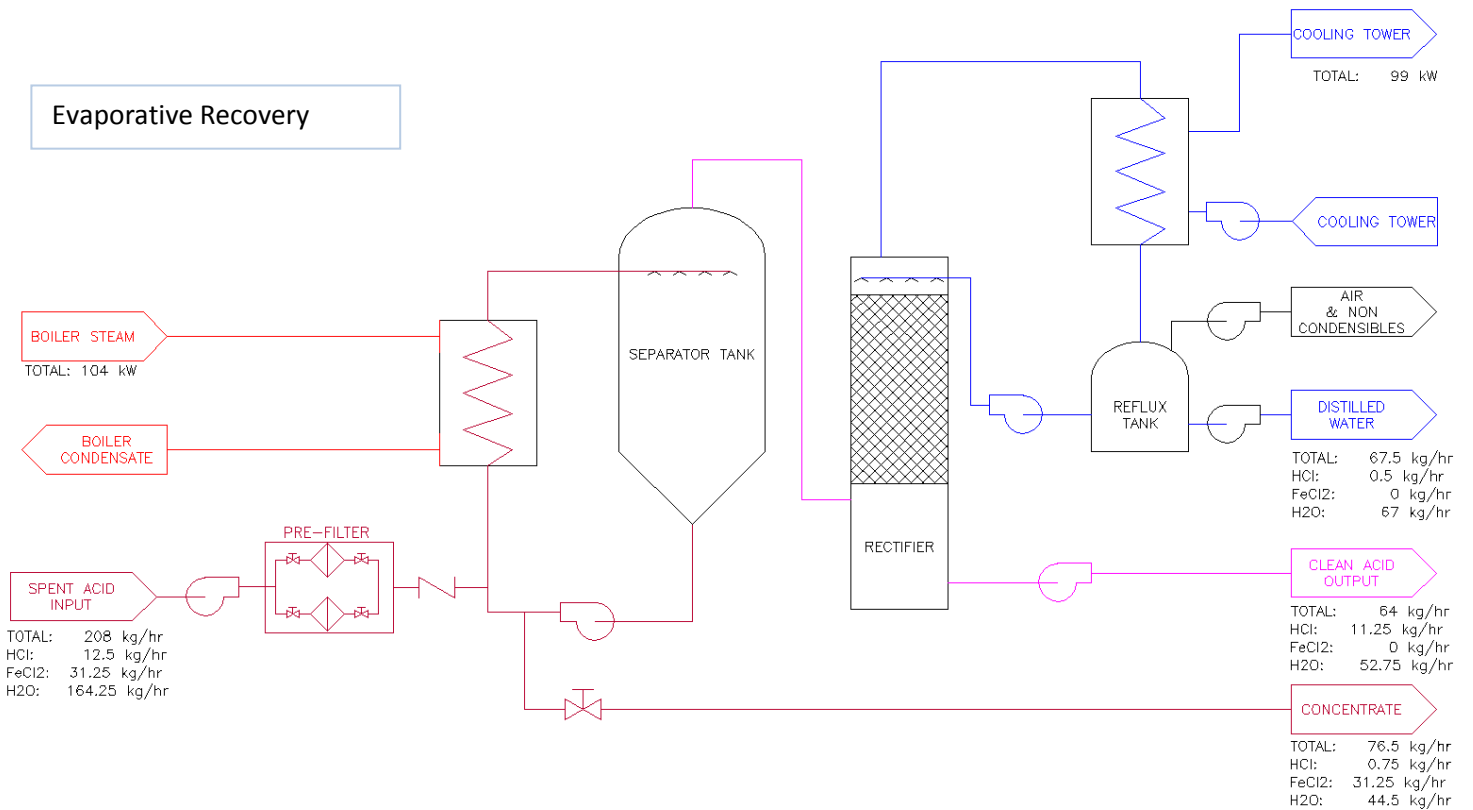
### Diffusion Dialysis



## Pyrohydrolysis

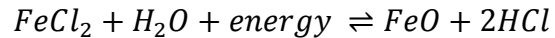


## Evaporative Recovery



### 3.0 Chemical Analysis

Mass balance comparison of the four different technologies reveals advantages in the categories of acid recovery, metals rejection, concentrate reduction, and acid concentration. Pyrohydrolysis excels in all categories which would be expected as pyrohydrolysis actively reverses the chemical reaction which takes place during the pickling process.



Pyrohydrolysis differs from the other technologies because instead of recovering the unbounded or “free” acid only, it breaks the bonds between the iron and chloride to produce iron oxide and hydrochloric acid. The concentrate/by-product is reduced by 91.5% and is discharged as powdered iron oxide (rust). It is important to note that the half reaction during the roasting process produces Hydrogen Chloride gas which will, in the presence of water, form hydrochloric acid. Hydrogen Chloride gas to hydrochloric acid is not always a complete reaction and will require special/additional scrubbing and/or air regulatory measures to ensure clean emissions.

Acid Sorption and Diffusion Dialysis, unlike Pyrohydrolysis and Evaporative Recovery, are not as energy intensive and have fewer components (see cost analysis). Literature on Acid Sorption and Diffusion Dialysis reveals high percentage returns on the amount of hydrochloric acid returned (not regenerated) from the spent acid stream: 80-90% for Acid Sorption (Cushnie, 2009, p. 246) and 80-95% for Diffusion Dialysis (Cushnie, 2009, 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). While Diffusion Dialysis 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, 2009, p. 278). Acid 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.

Pyrohydrolysis and Evaporative Recovery return acid at a concentration near the azeotrope (in this case 17.5%) and reduce the concentrate/by-product mass by 91% and 63% respectively. Although Evaporative Recovery requires more energy than Acid Sorption or Diffusion Dialysis, it requires less than half the energy of Pyrohydrolysis. The temperature of operation for a Evaporative Recovery system versus Pyrohydrolysis is significantly lower. Pyrohydrolysis temperatures are between 650°C and 950°C (Mach, 2013, p. 4) while a Vacuum Evaporative Recovery system does not exceed 80°C and an Atmospheric Evaporative Recovery system does not exceed 120°C. 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 shipping cost and higher resale value. An additional step is required to produce the ferrous chloride tetrahydrate.

## 4.0 Cost Analysis

Assuming the following rates for Utility and Operating Cost Calculations:

\$3.68 per MMBtu Natural Gas (U.S. Energy Information Administration, 2013)

\$0.099 per kWh Electricity (U.S. Energy Information Administration, 2013)

\$0.00073 per liter H<sub>2</sub>O (The Water Information Program, 2013)

\$85.43 per metric ton HCl at 33% by weight (ICIS, 2006)

\$1.18 per gallon HCl at 33% (ESTCP Cost and Performance Report: Spent Acid Recovery Using Diffusion Dialysis, 1999, p. 24)

\$70.00 per ton Lime (ICIS, 2006)

\$0.26 per pound Wastewater Treatment of Sludge (F006) (Cushnie, 2009, p. 361)

\$0.10 per pound Spent Pickle Liquor Recycling (Cushnie, 2009, p. 362)

Utilities Required	Acid Sorption	Diffusion Dialysis	Pyrohydrolysis	Evaporative Recovery
Electricity (kWh)	~4 (est.)	~4 (est.)	10 (est.)	6.34
Water (L/hr)	112.2	194	~5 (est.)	~5 (est.)
Natural Gas (MMBtu/hr)	0	0	0.819	0.355

Utilities Costs (\$/hr)	Offsite Disposal	Onsite Neutralization	Acid Sorption	Diffusion Dialysis	Pyrohydrolysis	Evaporative Recovery
Electricity	0	0.2	0.396	0.396	0.99	0.628
Water	0	0	0.058	0.10	0.01	0.01
Natural Gas	0	0	0	0	3.01	1.31
<b>Total Cost</b>	<b>\$0</b>	<b>\$0.2</b>	<b>\$0.454</b>	<b>\$0.496</b>	<b>\$4.1</b>	<b>\$1.948</b>

<b>Operating Cost*</b> (\$/year)	<b>Offsite Disposal</b>	<b>Onsite Neutralization</b>	<b>Acid Sorption</b>	<b>Diffusion Dialysis</b>	<b>Pyrohydrolysis</b>	<b>Evaporative Recovery</b>
Material	0	82	3,980	35,023	24,660	822
Labor	0	300,000	474,000	150,000	600,000	150,000
Utilities	0	1,200	2,724	2,976	24,600	11,687
Acid	146,400	146,400	88,800	91,680	1,200	92,400
Contamination Correction	0	0	44,527	55,396	2,822	0
Treatment	0	56,925	160	318	0	0
Disposal	278,437	182,711	50,895	88,151	23,364	100,980
Regulation	27,300	21,558	22,673	25,384	N/A	5,841
<b>Total Cost</b>	<b>\$452,137</b>	<b>\$708,876</b>	<b>\$687,759</b>	<b>\$448,928</b>	<b>\$676,646</b>	<b>\$361,730</b>

*\*Based on plant operation: 24 hours/day, 5 days/week, and 50 weeks/year*

### **Material Costs**

The specialized resin used to facilitate Acid Sorption is a primary material cost. Other common replacement materials include: pump seals and filters. Acid Sorption resin material has a life span of about 5 to 10 years for hydrochloric acid applications (Cushnie, 2009, p. 252). If insufficient filtration or extreme conditions occur, the life will be significantly shorter.

Membranes are the primary material cost for Diffusion Dialysis. Other replacement materials include: pump seals and filters. As in Acid Sorption, pre-filtration is exceedingly important in Diffusion Dialysis 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. Diffusion Dialysis membranes have a life span of about 5 years (Greiner Environmental, 1999, 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 creating an uneven flow distribution that can affect performance.

Pyrohydrolysis and 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. Due to the high temperature direct contact roaster in Pyrohydrolysis, a variety of components have a reduced life span. Many costs associated with Pyrohydrolysis are actually due to the gas scrubbing and building maintenance. The high temperature and iron oxide dust generated in the process can escape and spread the oxide powders over several acres. Containment is a very important part of the process.

## Labor Costs

The education and technical ability is about the same for Acid Retardation (Sorption) and Diffusion Dialysis 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. Pyrohydrolysis, due to its complex nature, number of components, and high temperature conditions, requires the most extensive training and significantly greater maintenance. Acid Retardation (Sorption), although a relatively simple operation in comparison to the other technologies, requires more frequent testing than Diffusion Dialysis and Evaporative Recovery and also requires more manual operations that will account for an increased labor cost.

## Utilities

Water and electricity are required for all 4 technologies. Water consumption is high for Acid Sorption and Diffusion Dialysis. It is relatively low for Evaporative Recovery and Pyrohydrolysis (Cooling Tower and Scrubber make-up water). Evaporative Recovery and Pyrohydrolysis have additional utility costs in the form of natural gas for the direct contact roaster involved in Pyrohydrolysis and the boiler in Evaporative Recovery.

## Acid

All 4 technologies return over 90% of the free acid present in the spent acid. Pyrohydrolysis goes a step further in creating additional hydrochloric acid by breaking the bonds in the ferrous chloride present. 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 combustion and waste processing.

## Contamination Correction

There needs to be a correction for the contamination of the return acid to the pickle tank. While all 4 technologies are designed for the same throughput, Acid Sorption and Diffusion Dialysis 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.

## Treatment

With the exception of Pyrohydrolysis, 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.

### Disposal

The cost of disposal will vary greatly depending on the region and regulation. For the purposes of this paper, we assume the following: neutralization performed onsite, sludge disposal by third party, and standard regulatory requirements for F006 waste. For a majority of Evaporative Recovery 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 Evaporative Recovery operations have been able to offload the resulting concentrate at zero or negative cost. Assuming a client is found, the disposal cost for an Evaporative Recovery operation is negated.

### Regulation

An average cost of regulation for industrial wire plants in the United States is tabulated for air and sewer. Acid Retardation, Diffusion Dialysis, and Evaporative Recovery have sewer costs associated with neutralizing the concentrate. Pyrohydrolysis has a different set of regulations associated with air quality. Due to the complexity of the regulations and changing EPA standards for air pollutants, the regulatory costs are only estimated. Air regulation for Pyrohydrolysis is known to have a considerable cost associated with its implementation.

## 5.0 Discussion of Issues Related to Ownership

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

**Acid Retardation:** In applications such as recovering Hydrofluoric and Nitric acid mixtures in stainless steel etching, this technology has flourished. The value of the acid (~10X HCl), cost of treatment and disposal, and the lack of competition justify the complexities of operation 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, 1997)

**Evaporative Recovery:** 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<sub>2</sub> 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.

**Pyrohydrolysis:** This technology is actually a small scale HCl manufacturing plant. It does not “recover” acid like the aforementioned technologies; it produces hydrochloric acid from the FeCl<sub>2</sub> salt. As a result, the yield of HCl from an equivalent ton of Spent Pickle Liquor is 55 -65% greater than the competing technologies. The mass of the by-product Iron oxide is also significantly less than the others since the water has been removed. Another benefit of the process is the use of rinse water in the rectifier to scrub the HCl gas into the hydrochloric acid. This novel use of rinse water eliminates the need to treat the waste rinse, causing only a minor increase in Fe contaminants in the recovered acid. In the wire industry, it is not common that the byproduct would be of high enough quality to sell to the largest consumers of this by-product. It is usually disposed of as a non-hazardous waste. The complex operation, environmental footprint, and high capital and operating cost usually limit this technology to very large consumers of HCl who benefit from the high recovery rate. Larger scale plants have a reasonable return on investment, but smaller scale operations usually look to other alternatives.



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