Acid Recovery Enhances Production & Reduces Costs

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Environmental protection equipment used to be classified as a "necessary evil" and logged into the financial statement as "overhead expense" between the entries for garbage and sewer. That classification has evolved over the past quarter century as environmental equipment has gained respectability and shares consideration with production equipment. In this new century of wireless global communication, laptop computers, and genetically designed food, production managers will brag about their recycling equipment in the same conversation they boast of their best production month. Not just because of an altruistic "green" philosophy, but because it has actually become more economical and productive to recycle than to dispose.

The reasons for the shift in paradigm have come over the past two decades. As the steel industry was faced with tougher effluent restrictions and increasing disposal costs, tighter resource management became necessary. The solution to these waste problems was multifaceted. The first step toward a solution required conservation of resources, thus minimizing waste. The second phase was to look for alternatives to the current practices and technology that could produce less pollution without negatively impacting production. The third phase was to look at the available technology for recycle to see if the waste could be recovered in the plant.

As Voltaire once stated, "No problem can stand the assault of sustained thinking." This observation proved true again as close scrutiny yielded positive results. An unexpected and happy surprise came when the internal audit revealed not only less wastes but also the unexpected bonus of improved production. By focusing on the "real" cost of pickling, process engineers found that they could speed up the pickling performance while greatly reducing waste and chemical consumption. The addition of recovery equipment to the process loop, increased production and allowed more options and innovation in the production process.

1.0 Waste Minimization -- Housekeeping

Waste reduction usually receives attention once a year when the corporate financial manager reveals the cost of disposal. But only a scientific study of the alternatives, followed by enforcement, can change a "culture" developed by the employees over a long period. Close attention to the actual costs of current practices followed by even closer study of alternatives will lead toward waste minimization. In many cases, one industry can benefit from the advances of another. The electroplating and circuit board manufacturing industries, for example, have developed very effective waste minimization techniques due to the extreme expense related to treatment of their hazardous and toxic wastes.

Effective rinsing, proper drainage, staging, pre-heating, and ventilation control are a few of the areas given minimal consideration during pickle line design. Unfortunately these areas impact both productivity and cost of production over the life of the plant. In all the areas mentioned, a dedicated junior engineer with a directive from management can produce most of the information necessary to optimize production and

minimize waste. Many times very expensive waste treatment plants can be reduced in size or even eliminated when waste reduction and recycling are practiced.

De-scaling technologies, such as mechanical de-scaling and electrolytic cleaning, are sometimes a good option for the smaller volume wire picking operations. The wire thickness, percentage and type of scale, and condition and alloy of the steel often limit the application of these technologies, however. Continued development of these alternatives is resulting in better engineering design and practices throughout the industry. Better competition produces greater innovation.

2.0 Optimizing Pickling and Choice of Pickling Agent

Medium and higher volume wire drawing facilities usually choose acid pickling as the most cost effective option of technologies available. The second question is which acid to choose: hydrochloric or sulfuric. The choice is usually related to cost, availability, and disposal cost; occasionally other factors such as tank heating, surface finish, and fuming are important. Hydrochloric acid dominates the international steel industry as the preferred pickling agent. The benefits of availability, ambient temperature activity, and more benign removal of oxides are cited as major reasons. Hydrochloric acid, by virtue of its method of attack on the oxide layer, generates a smoother, less pitted surface than sulfuric acid. When compared with sulfuric acid, hydrochloric acid also has the advantage of a longer active life. Sulfuric acid begins to lose effectiveness at about 80 grams per liter iron contamination whereas hydrochloric lasts up to 120 grams per liter before showing similar losses. The greatest single negative feature associated with the use of hydrochloric acid continues to be the corrosive vapors that attack the plant and personnel if the solutions are not ventilated and controlled properly.

In the United States, however, the majority of general wire picklers and galvanizers continue to use sulfuric acid despite the cost of heating the solution and its shorter useful life. One reason often cited is the ability to recover the acid. Today, over eighty percent of the wire and steel pickling plants in the U.S. who use sulfuric acid also recover it. Most have learned to balance their plant chemistry to minimize the cost of treating rinse water or disposing contaminated solutions. In short, they have closed the environmental loop while maintaining optimum production and profitability.

With the advent of cost effective hydrochloric acid recovery technology, these gains in productivity and profits can also be achieved without sacrificing the advantages of using hydrochloric acid.

Sulfuric Acid (10% at 70ºC)

Hydrochloric Acid (10% @ 35ºC)
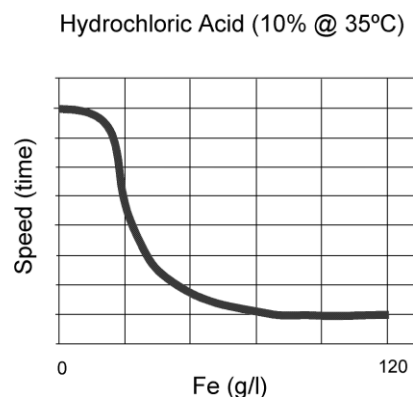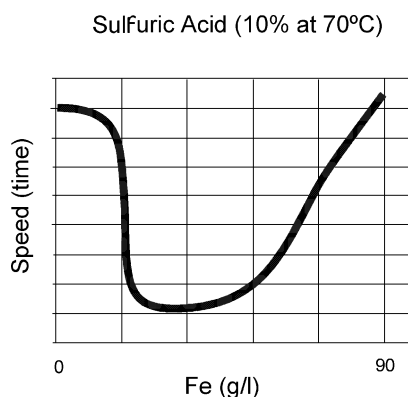
2.1 Pickling Speed vs. Iron Contamination

To better understand the relationship between pickling speed and iron contamination, we conducted a controlled laboratory study. The object of our experiment was to graph the pickling speed of similar squares of oxidized mild steel when immersed in a variety of concentrations of acid and iron. These experiments were then repeated at different temperatures to quantify any changes in the relationships. Although neither the composition nor the surface rust we pickled for laboratory purposes can directly reflect all actual steel oxide layers, it gives us insight into the mechanisms that affect the pickling process and shows us where the optimum bath chemistry parameters reside.

As shown by the graph, the existence of iron salts in the hydrochloric acid solution does not negatively affect the rate of pickling. Although it would seem counter-intuitive, a small amount of iron in solution must be present to catalyze the reaction. Fresh hydrochloric acid solutions without iron will actually pickle more slowly than near-spent, iron rich solutions. The reason for this may reside in the intermediate reaction of the acid with the iron oxide that creates ferric chloride as a transition molecule. Once formed, the ferric chloride quickly reacts with the base metal to form the ferrous chloride molecule that is stable in the acid medium.

Hydrochloric acid and sulfuric acid age differently. If the acid concentration of the pickling solution is constant, sulfuric acid will gradually lose effectiveness until it reaches its saturation point. Hydrochloric acid has a broader, flatter range of pickling activity until approaching saturation, and then any pickling quickly becomes protracted. In both cases, once the saturation point has been reached, iron salts begin forming on the surface of the work and inhibit further effective processing.

2.2 Temperature and Acidity Control

As the previous graph suggests, the available excess of hydrochloric acid impacts the saturation level of the iron in solution. Crystallization of ferrous chloride begins once the iron saturation level has been reached. As suspected, increasing the temperature of the solution extends the iron saturation point. Many picklers take advantage of this thermal principle of Chemistry by heating their hydrochloric solution when it approaches exhaustion.

This graph actually demonstrates the chemical law that states for every ten degree centigrade increase in temperature, the reaction rate doubles. The mirror image of this reflects the unfortunate result
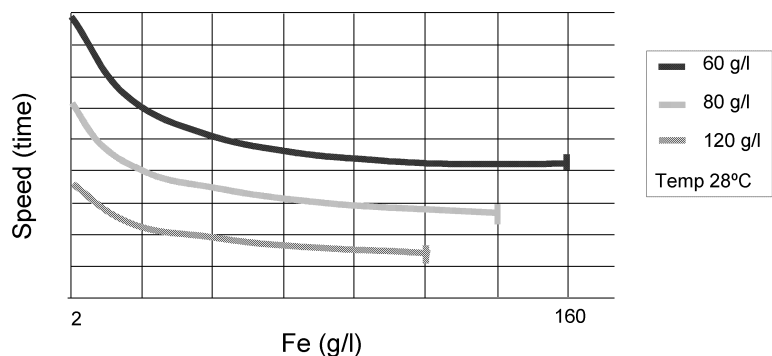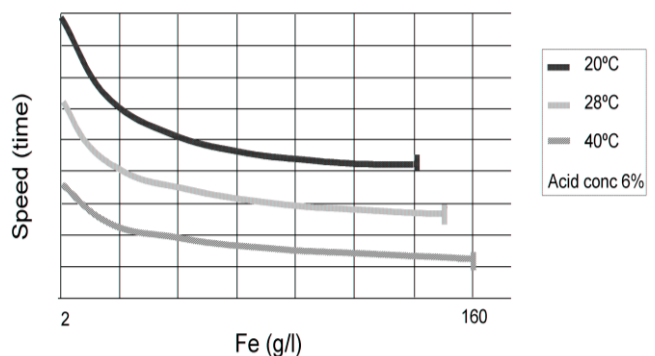
that hydrogen chloride vapor evolution rates also increase. Based on the need to navigate that narrow channel between pickling speed and acid vapor discharge, optimum pickling parameters have been developed. Steel pickling is routinely performed in a sweet spot where the bath temperature is kept between 25° and 40°C, and the acid concentration maintained below 120 grams per liter. This allows quick pickling with minimal off gas. Operating a hydrochloric acid pickling bath at acid levels above 100 grams per liter and 40°C requires ventilation and scrubbing.

3.0 Optimizing Pickling – Configuration of Pickle Line

The first step toward conservation of resources is evaluation of current practices and options. One North American wire producer conducted an in-house cost analysis that charted the most common pickling practices and came up with this comparison.

	Batch Pickling HCl: 16% to 5% w/v Fe: 0% to 12% w/v	Cascade Pickling HCl: 16% to 3% w/v Fe: 6% to 16% w/v	Batch + HCl Recovery HCl: 8% to 13.4% w/v Fe: 10% to 18% w/v
Fresh acid consumption (usg/ton)	6	5.7	4.5
Tons of 35% w/v HCl used per year	4,388	4,168	3,291
Cost of 35% HCl @ $80 per ton	$351,000	$333,450	$263,250
Gallons of waste acid per year	900,000	855,000	675,000
Disposal volume/year (usg)	1,800,000	1,380,000	890,000
Waste Disposal Charge per gallon	$0.325	$0.325	$0.000
Disposal cost per year	$585,000	$448,500	$0
Energy consumption			
Natural gas	n/a	n/a	$45,000
Electricity	n/a	n/a	$15,000
Maintenance cost			
Operation and Maintenance	n/a	n/a	$70,000
Depreciation			$40,000
Annual cost	$936,000	$781,950	$433,250
Cost per ton	$6.24	$5.21	$2.89

Disregarding other factors, the cost per ton of steel pickled marginally favors cascade pickling. Although the respective advantages of cascade, "leapfrog", or batch pickling remain a subject of debate, using resource recovery always reduces the cost of pickling and provides much better control of the pickling chemistry. Some of the comparisons are represented in the next section.

3.1 Comparison of Pickling Methods with and without Recovery

It is clear that batch pickling is the most expensive method of pickling with hydrochloric acid when no recovery is used. Batch pickling without recovery also requires many different complicated recipes for necessary immersion times due to the different levels of contamination of each acid pickling tank. Without agitation, this method requires longer pickling times due to the "nesting" problems where acid takes longer to attack scale where the coil limits acid access. The addition of acid recovery and coil agitation makes this method more competitive with the cascade options.
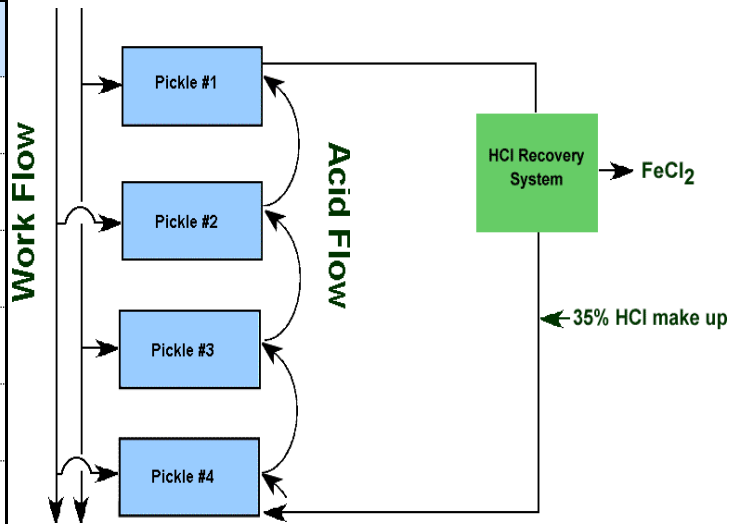
Batch	Batch with Recovery
1 pin transfer	1 pin transfer
variable immersion times with different chemistry	short immersion times with agitation, common solution
poor acid usage	excellent acid usage
no agitation	circulation agitation
many recipes	fewest recipes
$6.24 per ton	$2.89 per ton
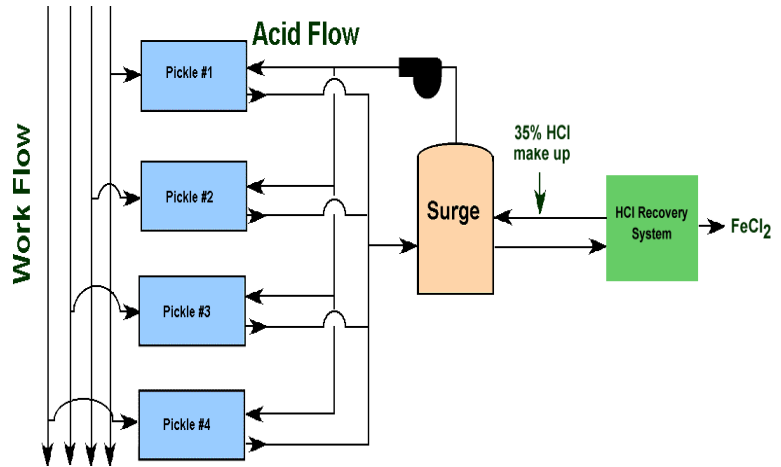
| Cascade	Cascade with Recovery
4 pin transfers	4 pin transfers
high immersion time	lower immersion time
Very good acid usage	Excellent acid usage
Agitation of coil by pin	Agitation of coil by pin
many recipes	fewer recipes
5.7 gal of 35% HCl / ton	4.5 gal of 35% HCl / ton
$5.21 per ton	$2.89 per ton
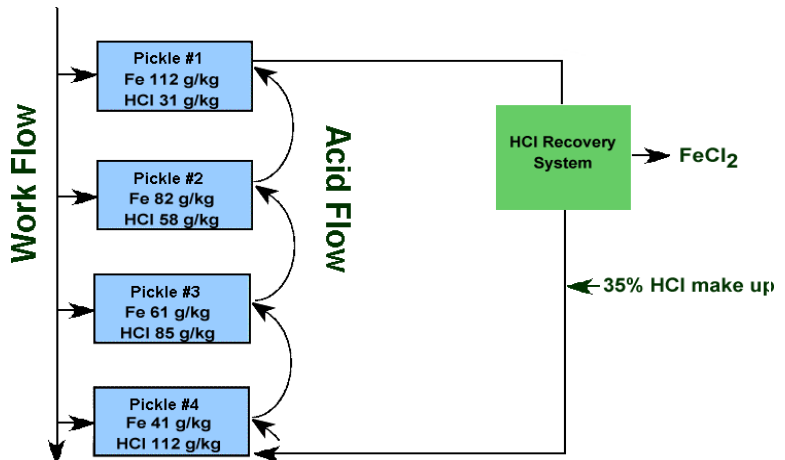
Cascade Leapfrog	Leapfrog with Recovery
2 pin transfers	2 pin transfers
medium immersion	Lower immersion time
Very good acid usage	Excellent acid usage
Moderate agitation	Moderate agitation
many recipes	many recipes
$5.21 per ton	$2.89 per ton

Work Flow

Acid Flow

Pickle #1

Pickle #2

Pickle #3

Pickle #4

HCl Recovery System → FeCl$_2$

← 35% HCl make up

A recent pickling philosophy favors cascade pickling by hypothesizing that the different forms of iron oxide require different relative concentrations of iron and acid in the pickling bath to efficiently remove different forms of scale. Advocates of cascade pickling argue that it takes less time to dip steel coil four times to attain excellent pickling than to dip the coil one time in a batch pickling tank and wait for all forms of scale to be removed. Our survey of over twenty steel plants using all methods of pickling suggests that pickling times appear to be more related to bath chemistry, levels of scale, bath operating temperature, and agitation. The multiple lifts necessary for cascade pickling seem to have the advantage of providing agitation through coil movement and thus solving scale residual problems left by "nesting" coil hanging from the hook. Many batch pickle operations have addressed this "nesting" problem by adding high volume, directed circulation or hook/coil vibration to force the acid between the nested strands. Placing a heat exchanger in the pump-circulation loop (below) and controlling the temperature of the pickling bath while forcing high volume circulation has resulted in faster pickling with fewer quality problems.

In summary, the focus on reducing environmental impact led to lower production costs and higher yields. Environmental legislation started a chain reaction that resulted in innovation, competition, and efficiency. The results have been positive for those who attacked the problem. Recovering the acid rather than disposing of it reduced production costs and generated valuable co-products. As one wise man once concluded, "We are continually faced with great opportunities brilliantly disguised as insoluble problems." Environmental problems fit this description.
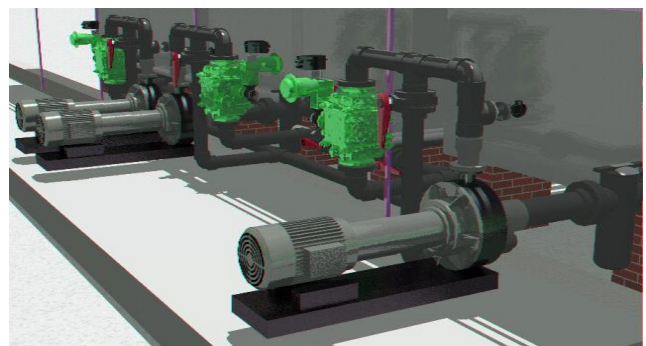
4.0 Optimizing Pickling – Tests on the Pickling Baths

A common problem in pickling is improper chemical analysis. Without a simple, reliable, repeatable set of tests the analytic results will vary from technician to technician. It will also make diagnosing pickling problems extremely difficult. Many chemical technicians use sodium hydroxide (NaOH) to titrate their pickling bath samples to determine the acid content. Unfortunately, sodium hydroxide forms insoluble iron hydroxide during the titration and produces erratic results. Many people use color changing indicators to determine the concentrations, but the endpoint of the titration will often be read differently by different chemical technicians producing differing results.

To solve these problems, we developed a few simple tests that are reliable and repeatable as well as inexpensive. *(See next pages.)*

4.1 Free Acid Test

Buret stand	Buret funnel, small	pH buffers – 4 & 7 pH
25 ml buret	1 ml sample dispenser	Reagent: sodium carbonate 0.2N
250 ml beaker	pH meter & pH electrode	

Procedures:

a.   Add 1 ml of sample to 50 mls water and mix.

b.   Add Sodium Carbonate (0.2 Normal) from buret, monitor pH and adjust to between 3.7 to 4.0.

c.   pH will change very slowly at first, depending on acid concentration, then will change with every drop.

d.   Record the volume (in mls) of Sodium Carbonate (titrant).

Reagent:

Total acid titrant   Sodium Carbonate (0.2 N)

Dissolve 10.6 grams of reagent grade Sodium Carbonate in 1 liter of water. Refrigerate.

Calculations:

Hydrochloric Acid Content (g/l) = (N or Normality of titrant) x (36.5) x (volume of titrant in mls)

Sulfuric Acid Content (g/l) = (N or Normality of titrant) x (49) x (Volume of titrant in mls)

% Acid = Acid Content (g/l) / Specific Gravity / 10

4.2 Iron Test

Buret stand	Buret funnel, small	Reagent: potassium permanganate 0.1N
25 ml buret	1 ml sample dispenser	Reagent: sulfuric acid 50%
250 ml beaker	5 ml acid dispenser or syringe	

Procedures:

a. Take 1 ml of the sample. Add to 50 mls water.

b. Add 5 mls of 50% Sulfuric Acid to sample.

c. Add Potassium Permanganate from buret until pink color appears (use a white background for the best detection results.)

d. Record the volume (in mls) of Potassium Permanganate (titrant)

Calculations:

Iron Content (g/l) = (Volume of titrant in mls) x (5.547)

% Iron = Iron Content (g/l) / Specific Gravity / 10

Reagents:

a. Iron titrant   Potassium Permanganate (0.1 N, 0.02 M): Dissolve 3.22 grams of Potassium Permanganate in 1 liter of water. Store in a dark glass bottle.

b. Iron buffer solution   50 % Sulfuric acid: Add 270 mls of concentrated Sulfuric acid to 500 mls of water. Add acid slowly so that solution does not boil.
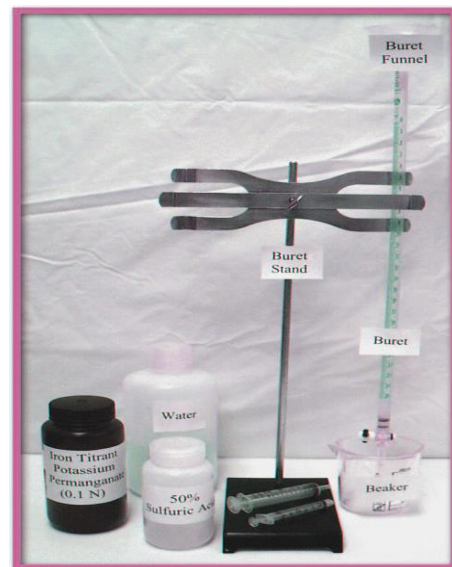
4.3 Specific Gravity Test

500 ml graduated cylinder
1.00 – 1.60 hydrometer
Reagents: none

Procedures:

Fill the graduated cylinder to 500 ml with diluted sample from acid test.
 Allow solution to cool to room temperature and then place the hydrometer in solution.
Read the specific gravity from the hydrometer scale.

5.0 Integration of Environmental Equipment and Production

The use of sulfuric acid recovery systems has reached a very high level in steel pickling over the past twenty years. The co-product, ferrous sulfate, has been marketed successfully during that time and has become the dominant source for the crystalline salt used in sewage and potable water treatment worldwide. Recycling systems such as "roasters" have been used in the large steel pickling plants, but their very large capital cost has limited their use in most wire and all galvanizing plants. The "roaster" co-product, iron oxide, is used as a paint pigment additive and to produce ferrite magnets.

In the past five years evaporative recovery of hydrochloric acid has become a very cost effective alternative to "roaster" technology for the small and middle sized pickling plants. The co-product of the hydrochloric evaporative process is ferrous chloride concentrate that is marketed like the ferrous sulfate. The ferrous chloride can easily be converted to ferric chloride through the addition of chlorine. The resulting ferric chloride has several additional markets such as the use as an etchant for circuit boards, flocculating agent for water treatment, and for treatment for phosphates in sewage.

The capital cost of the different technologies has been reduced over the past decade due to technological advances, competition, and expanded use. The markets for the co-products have followed the expansion of the use of these technologies. The co-products are used worldwide and are sold through chemical brokers and sometimes directly from producers to end users. What was once a hazardous waste has become a tool to combat pollution.

Oliver Wendell Holmes, an American jurist and philosopher, once surmised, "Man's mind, once stretched by a new idea, never regains its original dimensions." As the steel industry focuses on solving its problems and produces truly innovative and cost effective solutions, it is unlikely that it will ever regress to its earlier practices. The beauty of the competitive marketplace is that industry simply cannot afford to step backward.