

## **An Ecologically Sound Solution to Dumping Waste Pickling Acid**

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### **I. Introduction**

Beta Control Systems, Inc. is a research and development corporation dedicated to the development of resource recovery equipment for industry. Our primary products recover chemicals used in the surface finishing of metals. Our acid recovery systems alone recycle nearly 1,600,000 liters of acid each day. As the world becomes more aware of the environmental damage generated by the disposal of spent acids and their sludge waste products, we expect recycle and recovery to become the only acceptable method of dealing with this waste problem.

In North America, environmental restrictions on the disposal of hazardous wastes have increased the cost and liability of handling spent acid to such a high level that recovery of the acid at the source is both environmentally and economically preferred. In industries such as wire and galvanizing, the majority of the users of sulfuric acid have converted from disposal or neutralization to point source recovery. As the cost of the technologies for recovery of other acids decreases, we expect to see an even greater movement toward point source recovery.

### **II. Acid Recovery Technologies**

#### **A. Evaporative Recovery for Hydrochloric Acid**

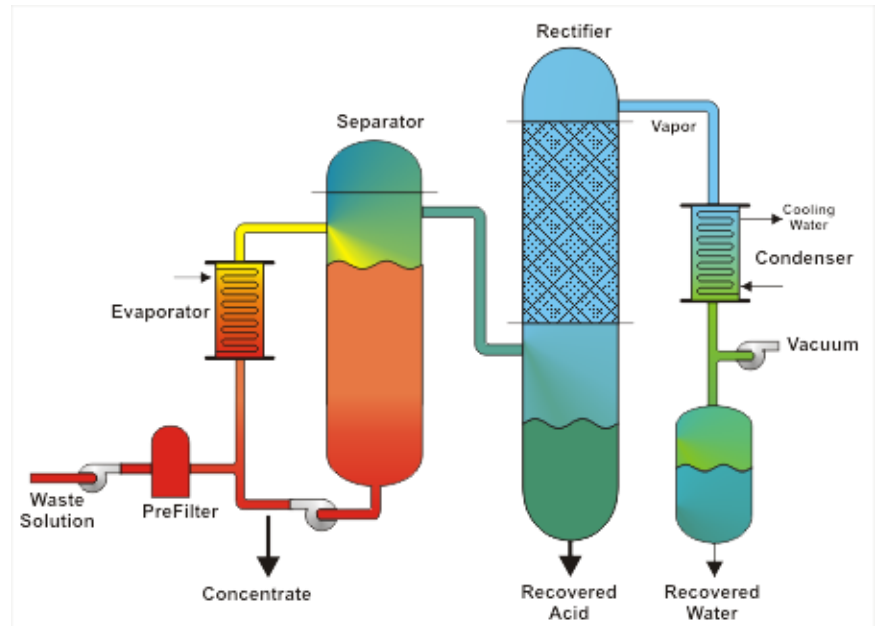
This technology is most commonly applied to acids that are active at room temperature, such as Hydrochloric. With Hydrochloric Acid, this technology returns an excellent, concentrated acid with very low metallic contaminants. It also produces a concentrated by product which can be sold as a liquid for use in municipal waste treatment facilities.

"Spent" hydrochloric acid ranges between 12% and 18% iron concentration when it no longer actively pickles. The residual acid concentration varies from 1% to 10%, depending upon the application. This leaves in excess of 60% of the remaining solution as water. The evaporative process aggressively heats the solution and extracts the acid and water from the "spent" waste. Only a super concentrated iron chloride solution remains.

## Flow Diagram: Hydrochloric Acid Recovery System

A pump forces the waste acid through a pre-filter and into the evaporator loop, comprised of the Evaporator exchanger and the Separator tank.

In the evaporator loop, the HCl and water vaporize as they travel through the heat exchanger and are released into the liquid/vapor Separator. The remaining metal salt solution (metals + H<sub>2</sub>O) continues to circulate through this pressurized boiling loop until it reaches a controlled concentration and is withdrawn to a storage tank.



Forced by expansion, the acid and water vapors are driven from the Separator and into the Rectifier. The concentration of acid is controlled in this step to return excellent quality, recovered acid to the process tank.

The remaining water vapor, stripped of acid, continues its journey into the Condenser where it is sub-cooled and condensed to nearly pure water. This water is reused as rinse water or is returned to the process tank with concentrated acid.

Until recently, the cost of building an evaporative recovery process to handle smaller industrial volumes of hydrochloric wastes was excessive. Advances in "super plastics," automated controls, and new fabrication techniques, however, have lowered the costs to make this technology much more affordable.

### B. Freeze Crystallization for Sulfuric Acid

This technology processes acids that are active at elevated temperatures. Increasing the temperatures of acids like Sulfuric, extends the activity and life of the acid. Commonly, sulfuric acid is heated to approximately 70°C for best pickling. At this temperature the acid is capable of dissolving up to 9% iron before pickling activity ceases.

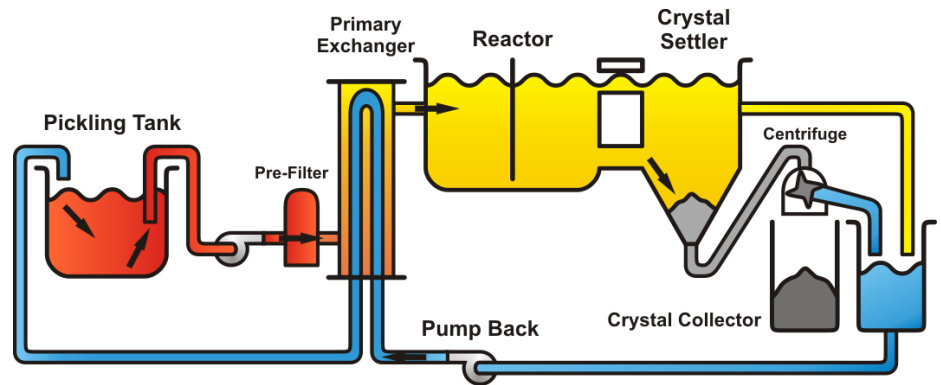
Once the pickling solution is spent or dead, the contaminating iron concentration can be significantly reduced and the pickling capacity regenerated through freeze crystallization. By adjusting the acid concentration and reducing the temperature, the iron in solution precipitates as a crystal. Properly

designed equipment will efficiently chill the acid as well as yield the greatest removal of crystal iron sulfate from solution. The recovered acid is then pre heated and returned to the pickling tank for further use.

The iron is removed in the form of crystalline Ferrous Sulfate Heptahydrate which has a variety of agricultural and commercial uses. In North America, the by product is sold as a commodity and can often produce enough revenue to offset the cost of operating the equipment. In any case, the Ferrous Sulfate crystals are not hazardous and are easy to handle.

#### Flow Diagram: Sulfuric Acid Recovery System

Pickling acid is drawn from the tank by means of a chemical pump and fed through a Pre-filter to remove suspended particles. Once the acid solution has been filtered, it passes through the Primary Exchanger, a thermal interchanger.



In this heat interchanger the temperature is reduced by using the previously cleaned chilled acid traveling counter-currently through the interchanger. In this way the chilled recovered acid is pre-heated and the hot spent pickle liquor is chilled without using an external energy source. This greatly reduces operating costs.

After the acid is pre-chilled, it enters the Reactor where the spent pickle liquor is agitated and chilled further until the iron forms an iron sulfate crystal (ferrous sulfate heptahydrate). The special thermoplastic heat exchangers immersed in the solution pass a refrigerant through the inner tubes that absorbs heat from the solution and displaces it through an air-cooled chiller. An acid resistant alloy agitator keeps the crystals from forming a cake of solid crystal on the exchangers by efficiently moving the solution across the exchange tubes.

The resultant chilled acid/crystal slurry enters the conical-bottomed Crystal Settler where the iron sulfate crystals quickly settle to the bottom and the clear, iron-reduced acid solution overflows into a pump station. The settled crystals are then pumped to a Centrifuge. The Centrifuge separates the thick crystal slurry into a dry ferrous sulfate crystalline product and a centrate solution of acid and crystal fines. The centrate is returned to the Reactor where the ferrous sulfate crystalline fines act as seeds to grow larger iron crystals. The clarate overflow of recovered acid is pumped through the Primary Exchanger where it is heated and returned to the pickle bath as excellent quality pickle liquor.

### III. Economics

Deacero, S.A. de C.V., a Monterrey, Mexico based manufacturer of steel wire products, purchased a 20,000 gallon per day sulfuric acid recovery system for their Saltillo plant. As a result, Deacero no longer pays to dispose their waste sulfuric acid. Instead they produce and sell high quality iron sulfate crystals, the by-product of freeze crystallization technology applied to sulfuric acid. In this real life example, management's conscientious effort to blend sound business practice with environmental concerns, serves to protect the company's profitability and the future of the surrounding community.

Deacero, and other companies with environmental technologies such as acid recovery, experience a payback time between nine months and two years. Variables influencing return on investment include: disposal, labor, transportation, and energy costs. Since these variables can radically differ from region to region, Return on Investment analysis should be calculated on a case by case basis.

The capital costs of an acid recovery system range from \$130,000 to \$500,000. Many larger plants have systems attached to each pickling line or will cross connect several pickling lines to one or more recovery systems. The compact design minimizes the cost and difficulty of installation. Most systems are installed for less than 10% of the capital cost of the equipment.

#### Before Resource Recovery

Yearly disposal cost prior to acid recovery:

96,000 gallons at \$2.05/gallon = \$196,800

(includes disposal fee, trucking, regulatory fees, and super fund tax)

#### After Resource Recovery

Purchase cost of Acid Recovery System \$213,292

10 yrs. straight line depreciation = \$ 21,329

Operating costs

a. Electricity at \$.03/KWH \$ 2,350

b. Filters 1,200

c. Bags or containers 1,280

d. Operation labor 7,000

\$ 11,830

Total cost/year with Acid Recovery \$ 33,159

**Yearly Savings with Acid Recovery \$163,641**

**Investment Payback on investment of \$213,292 = 1.3 years**

#### **IV. Conclusion**

As environmental consciousness expands throughout the world, the critical focus on the metals industry sharpens. Resource recovery becomes not an option but a mandate. "Dirty" industries become unwelcome, and offending companies face forced closure. International trade agreements will require environmental compliance and certification by exporting companies. No manufacturer will be immune to scrutiny.

Fortunately there are economical alternatives. There are reliable processes available to recover both waste and reputation as a non polluting industry. Development of recycling technologies continues at a rapid pace, and soon resource recovery equipment will become as much a necessity as any other piece of production machinery. In plants, like Deacero, that have already implemented their resource recovery plans, this is already so. And they continue to reap the economic and public relations benefits of their actions.



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