Zero Discharge Pickling -- Sulfuric or Hydrochloric

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1.0 Introduction

Voltaire stated, "No problem can withstand the assault of sustained thinking." The problem of preserving our environment while utilizing the earth's resources has created conflict since man first discovered fire. As large users of hazardous and dangerous chemicals, the galvanizing industry shares this dilemma. Members of this industry have addressed the need to minimize, recover, or recycle sulfuric and hydrochloric acids used in the pickling of steel over the past decades, but most of the technologies available were simply too expensive to own and operate. So the assault of "sustained thinking" continued.

Within the last twenty years, new developments in materials technology, inexpensive process automation, and novel approaches to energy recovery have given acid recovery a rebirth. New thermoplastic fabrication materials, carbon based composites, and unique heat exchanger designs merged to provide recovery systems that withstand extremes of temperature and corrosives while remaining mechanically and economically sound.

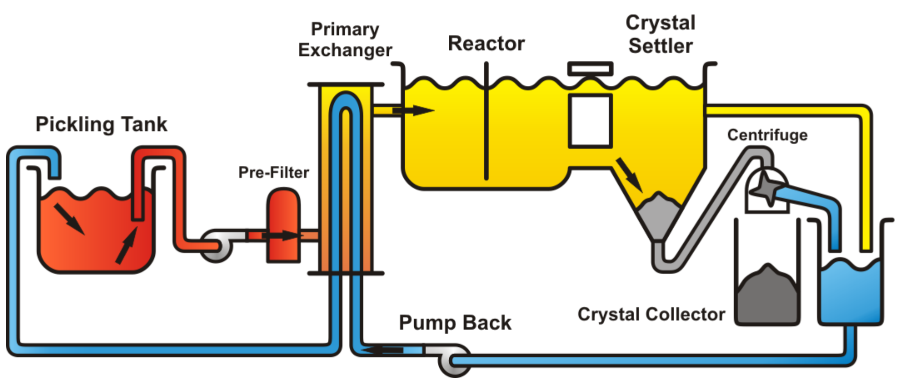
2.0 How Recovery Technologies Work

Each steel part that is dipped into a pickling bath adds to the dissolved metals in solution. Metal concentrations rise until the pickling rate slows to an unacceptable degree. At this stage an acid pickling solution is spent or dead. The contaminating iron and zinc concentrations can be significantly reduced and the pickling capacity regenerated with a recovery system.

With freeze crystallization technology, the temperature of the incoming acid is reduced to promote metals precipitation. With evaporation technology, the temperature is elevated to evaporate the water from the incoming acid. Properly designed equipment will efficiently chill or heat the incoming acid as well as yield the greatest removal of iron and zinc from solution. The recovered acid will be suitable for return to the pickling tanks.

2.1 How a Sulfuric Acid Recovery System Works (Freeze Crystallization)

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.

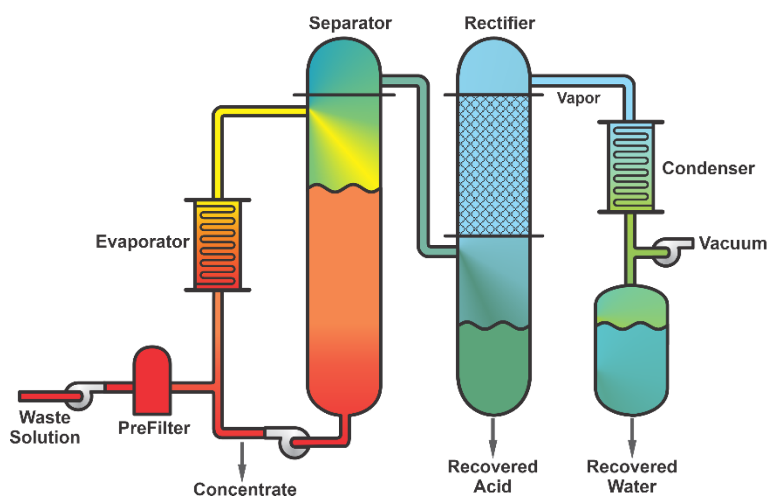
After the acid is pre-chilled, it enters the Reactor where the spent pickle liquor is agitated and chilled further until the iron forms an iron sulfate crystal (ferrous sulfate heptahydrate). The special thermoplastic heat exchangers immersed in the solution pass a refrigerant through the inner tubes 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.

2.2 How a Hydrochloric Acid Recovery System Works (Evaporative Recovery)

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

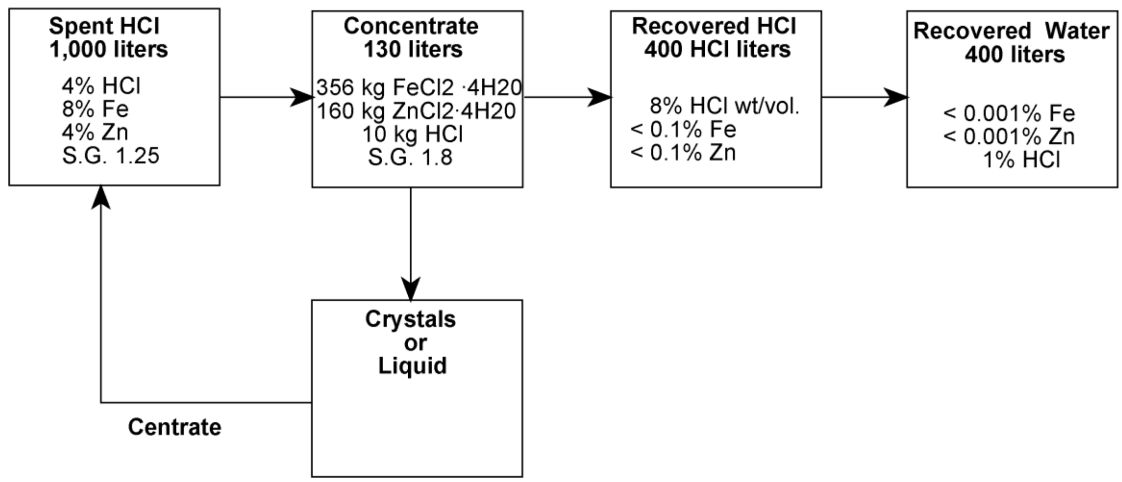
In the evaporator loop, the HCl and water vaporize as they travel through the heat exchanger and are released into the liquid/vapor Separator. The remaining metal salt solution (metals + H_2O) continues to circulate through this pressurized boiling loop until it reaches a preset concentration and is 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 excellent quality water. This water is reused as rinse water or is returned to the process tank with concentrated acid.

3.0 Example of Hydrochloric Acid Recovery Mass Balance. Where do the Chemicals go?



To illustrate the process, we can follow 1,000 liters of a galvanizer's spent pickling acid through the system.

Chemical analysis of 1,000 liters of the spent HCl:

4% Hydrochloric Acid	8% Iron	4% Zinc	1.25 specific gravity

The 1,000 liters of solution is evaporated to 130 liters of concentrate:

356 kg $FeCl_2 \cdot 4H_2O$	160 kg $ZnCl_2 \cdot 4H_2O$
10 kg HCl	1.8 specific gravity

Chemical analysis of recovered Hydrochloric Acid:

400 liters of 8% HCl wt/vol.	< 0.1% Fe	< 0.1% Zn

Chemical analysis of recovered water:

400 liters of water	< 0.001% Fe	< 0.001% Zn	1% HCl

The balance of volume is the differences between the specific gravity of the concentrate, the incoming temperature, and the final sub cooled temperature.

The recovered acid can be returned to the pickling tub. Additional virgin acid blended into the pickling tub will make up for losses in the pickling process.

The recovered water can be used in the rinse tank or in the pickle tubs to dilute the virgin acid required to replace the spent acid.

4.0 Closing the Loop for HCl Recovery

In most steel pickling, countercurrent/cascade rinsing has proven the most efficient method. It allows excellent rinsing with the lowest consumption of water. The use of a simple conductivity controller and the training of personnel in dipping and draining technique, can minimize water consumption without sacrificing product quality or introducing chemical cross contamination.

It is important to note that rinse tubs require vigorous agitation to achieve complete mixing. Locating the incoming water feed near the bottom of one end of the tub and the overflow weir at the opposite end, will ensure complete mixing and avoid short circuiting. Addition of an air sparge into the tub will often provide this agitation simply and inexpensively.

Both theory and practice have proven that properly executed multiple countercurrent rinsing will result in a reduction in water usage of greater than 90% compared with single tank overflow rinsing. Combining multiple counter-current rinsing with evaporative recovery of the rinse overflow will close the loop on the entire acid rinse process.

The evaporative system can store and process the rinse overflow from a multiple (two or more) cascade/counter-flow rinse, returning the recovered water to the final rinse tank. The small volume of ferrous chloride removed from the rinse stream is added to the spent hydrochloric acid solution. Other options exist that do not include use of a storage tank, but we have shown one for the purpose of illustration.

5.0 Energy Consumption with HCl Recovery

The evaporative hydrochloric acid recovery system is technically a forced circulation flash evaporator with controlled two stage condensation/separation. In addition to these important stages of chemical separation, we have included a unique tube plate interchanger. This interchanger exchanges sensible heat from the HCl and water vapor with the spent acid at room temperature which is fed into the system. In this manner, the interchanger saves approximately 150 KW during the heating and cooling phases.

A system processing 25,000 liters of spent hydrochloric acid per day will use the following energy:

480 KWh/day electrical	($9 - $18 USD)
1,500 - 2,000 m^3 of natural gas	($200 - $300 USD)

The energy cost in U.S. dollars is approximately $8.75 to $12.25 for every 1,000 liters processed. This cost is based on proper insulation, steam condensate return, and continuous operation. If available, a waste heat source can further reduce energy consumption.

6.0 Operation and Maintenance

Operation of the process is very simple. After a 30 minute start up procedure to bring the system up to temperature, the operator performs periodic checks on the system throughout his shift. The operator remains free for other plant duties and should not feel attached to the process.

The Programmable Logic Controller (PLC) sends operating information and alarm messages to a remote display to alert the operator or supervisor to any abnormal conditions. If the system enters an extreme situation, it will automatically shut down, sound an audible alarm, and display a flashing light demanding attention.

Normal maintenance of the system includes changing filters, occasional attention to pumps, and checking the boiler and cooling tower loops to ensure optimum performance. The process also has an information display that alerts the operator/maintenance person to energy losses or problems, as well as suggested actions to solve them.

7.0 Conclusion

The Beta resource recovery systems are often considered an integral part of the production process while performing an important environmental task. Recovering resources at the source has proven both economically and philosophically advantageous. By continuously removing contaminants from the pickling solution and operating with improved quality rinse waters, processing times shorten and quality improves. Concurrently, the costs associated with environmental compliance are greatly reduced.

A wise man once said, "When the well is dry, we will know the worth of water." The savings from resource recovery are measured in more ways than just energy and labor costs against disposal costs. When resources are wasted or turned into hazardous materials, they will never be returned. Waste generating disposal methods that appear simple and inexpensive today may prove enormously expensive in the near future.

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