CAPSULE REPORT

RECOVERY OF SPENT SULFURIC ACID FROM STEEL PICKLING OPERATIONS

PREPARED BY U.S. ENVIRONMENTAL PROTECTION AGENCY ENVIRONMENTAL RESEARCH INFORMATION CENTER
Acid recovery tower (left), acid mist filter (center), fresh acid storage tank (right)
Approximately 100 million tons of steel are produced every year in the United States. A large portion of this steel is initially produced in some intermediate form, such as sheet, rod, or ingot, and then sent to other manufacturers for further processing into final steel products. During the manufacturing process as well as during the storing and shipping of the intermediate forms, the steel develops a surface coating of oxidized iron which must be removed before the steel can be processed further.

The removal of the surface scale through a chemical reaction of the scale and steel with sulfuric (H₂SO₄) or hydrochloric (HCl) acid is called pickling. Sulfuric and hydrochloric acids are the major acids used in the pickling process, although other acids may be used. In the pickling process the steel is immersed in an acid bath which dissolves the scale and some of the iron. After a required period of time, the steel is removed from the acid bath and the residual acid is rinsed from the steel. As the iron content in the pickling acid bath increases, the pickling efficiency is reduced and fresh acid must be added to the bath to maintain an efficient reaction rate. Eventually, the iron content becomes excessive for effective pickling, and the “spent pickle liquor” must be replaced with fresh acid.

It is estimated that about one-half of the steel produced in the United States is cleaned by the pickling process. The disposal of this spent pickle liquor and the associated rinse waters creates a pollution problem for the manufacturer. The sources of the wastewaters and the types of treatment technologies are shown in Figure 1.

![Figure 1. Handling Pickling Acid Streams](image-url)
The large primary manufacturers of steel products generally use hydrochloric acid in the pickling process. Sulfuric acid is used by the smaller, secondary steel finishers. Although the amount of steel pickled by hydrochloric acid is approximately twice the amount pickled by sulfuric acid, the number of facilities using sulfuric acid for batch pickling far exceeds those using hydrochloric acid.

The nation-wide control of this source of pollution is complicated by the large number of manufacturers using relatively small amounts of sulfuric acid. The spent sulfuric acid pickle liquor, totaling about 375 million gallons per year, is highly concentrated, containing up to 10 percent dissolved iron and up to 10 percent unreacted sulfuric acid. The rinse water used to remove the residual acid also adds to the volume of contaminated wastewater. The following are four major methods that are used to control pollution caused by sulfuric acid pickling.

- **Acid Recovery** — The dissolved iron salts are removed from the spent acid, which then can be reused.
- **Neutralization** — A base (usually lime) is reacted with the spent acid, which is then discharged.
- **Contract Disposal** — For a fee, a contractor takes the spent pickle liquor from the manufacturer and finds a method for disposal.
- **Deep Well Injection** — The pickle liquor is injected deep into the earth, where it is contained between impervious layers of rock.

This report is intended to provide small manufacturers using sulfuric acid pickling with the technical and economic information necessary to select the treatment technologies best suited for their facilities. Because deep well injection has only limited application, to these plants, it is not discussed in this report.
**2. THE ACID RECOVERY PROCESS**

*Basic Principles of Operation*

There are several different commercially applied processes for recovery of sulfuric acid from spent pickle liquor. All processes, however, rely upon the basic principles of crystallization of iron salts (mainly ferrous sulfate) from the spent liquor and the addition of enough fresh sulfuric acid to return the pickling solution to its original acid strength. These commercial acid recovery systems allow the free sulfuric acid remaining in the spent pickling solution to be reused. However, they do not regenerate sulfuric acid from the iron salts obtained in the reaction with the steel.\(^1\) The processes differ in the methods used to crystallize the ferrous sulfate.

\(^1\)Although there are processes under development which do regenerate sulfuric acid from these iron salts, the economics for commercial application have not yet been proven.

The solubility of iron salts in pickle liquor is such that crystallization can be induced by cooling or by evaporating water from the solution. Commercial processes are available which use either of the above techniques, as well as combinations of the two. In addition, both batch and continuous processes are available. The selection of the best process for a specific pickling operation depends upon several factors, which will be discussed in Section 4.

Figure 2 illustrates the basic principles of a batchwise cooling process, a system widely used by smaller facilities in the United States. In this illustration, the acid recovery unit is integrated into a wire production facility.
When the dissolved iron and the sulfuric acid content of the pickling solution reach a predetermined level, it is pumped to the batch crystallizer. The pickling tank is then immediately recharged with recovered acid from a previous batch, and pickling resumes.

The crystal yield can be enhanced by adding fresh sulfuric acid to the crystallizer at this time. Since the make-up acid is at a high concentration, the solubility of the ferrous salt is reduced, and a higher yield is obtained. The disadvantage is that heat of dilution must be removed by the refrigeration unit.

In the crystallizer, over a period of 8 to 16 hours, the temperature of the spent liquor is slowly reduced to a temperature between $35^\circ$ to $50^\circ$F. During this cooling cycle ferrous sulfate heptahydrate (FeSO$_4$•7H$_2$O) is crystallized from the solution.

The ferrous sulfate crystal slurry is transferred into a crystal collection chamber which retains the crystals but allows the pickle liquor to pass through to an acid recovery tank. The retained ferrous sulfate heptahydrate crystals are then washed with small amounts of fresh water to remove free acid. The water adhering to the crystals is partially removed by drawing air through the crystal bed. The resulting ferrous sulfate crystals are removed for disposal, or, preferably, marketed. The recovered acid is preheated using steam, and is ready to be returned to the pickle liquor tank.

The net effect of the acid recovery system is to recover the unreacted sulfuric acid for reuse, instead of discharging it as a waste product. Additionally, the ferrous sulfate crystals are recovered in a form which usually can be marketed.$^1$

In this batch system, cooling is provided to the spent liquor by circulating chilled water through cooling coils. Teflon® heat exchange coils often are used as a cooling surface, since coating and corrosion of metallic cooling coils can be a problem.

Other processes differ from the one described only in the methods used in the crystallization step and in the separation of the formed crystals from the recovered acid. One continuous process uses a vacuum crystallizer. By decreasing the pressure in the vessel to 28 in. Hg. vacuum, the pickle liquor is cooled and a portion of the water is vaporized.

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$^1$ Ferrous sulfate is used as a coagulant in municipal waste-treatment plants, as a fertilizer additive, animal feed additive, pigment production, and as a raw material for iron oxide in magnetic tapes.
crystals are discharged from the crystallizer body to a centrifuge which separates and washes the crystals from the liquor. The liquor is returned to the pickling tank and the crystals are sold or stored.

**Adapting Acid Recovery to the Pickling Process**

If acid recovery is to be used to minimize or even eliminate the discharge of wastewater in an existing pickling facility, normally it will be necessary to reduce the amount of water being added to the pickling system. If this is not done, the efficiency of the recovery system is impaired. Ideally, in a zero discharge condition, the water leaving the system through free moisture and the water of hydration of the crystals combined with the evaporation occurring during the pickling process will equal the water being added.

There are three major sources of added water in the pickling process: (1) large amounts of water often are used for rinsing the pickled steel; (2) the common technique of using live steam injection as a means of heating and agitating the pickling solution adds water as condensed steam to the pickle liquor; and (3) some water is produced by the reaction of the iron oxide scale with sulfuric acid.

The most common method for reducing the rinse volume is through counter-current contacting of the work and the rinse water. One of the least expensive techniques to do this for batch pickling is to use the dip and spray system shown in Figure 2.

After dipping in the rinse vessel, a spray of fresh water is applied to remove the slightly contaminated rinse water remaining on the steel. The slightly contaminated spray water then falls into the rinse tank. The more concentrated water from the rinse tank eventually is transferred to the pickling tank, where evaporation further reduces the water volume.

To eliminate the dilution of the pickle liquor by condensate, the live steam injection for heating the pickling solution is replaced with a steam heat exchanger, which prevents steam from contacting the pickle liquor.

The use of direct steam injection as a method for heating and agitating the pickling bath developed because of the corrosiveness of the pickling solution and its tendency to coat heat transfer surfaces. However, the dilution effect of the steam condensing in the pickle liquor made recovery of the acid very difficult. Teflon® coils, which prevent the heating steam from contacting the pickle liquor, can be used as heat exchangers. Air injection can then be used for agitation, which results in improved pickling rates. This air also maintains the negative water balance for the plant, since water evaporation from the pickling tank is improved by the air flow.\(^1\)

Some wire mills have achieved zero discharge of wastewater from the pickling plants by installing an acid recovery system and by modifying the pickling line to include staged rinsing, indirect heating and air injection agitation to reduce water usage. Because zero discharge will require additional investment for the modifications and an exact balancing of water rates, each plant must examine the operating costs and economics for its situation. This is discussed further in Section 4.

\(^1\) This increased evaporation does require some additional steam.
Neutralization

Neutralization has been the traditional method for treating acid streams, and it has been used for dilute pickle liquors. There are many possible neutralizing agents, such as caustic soda, soda ash, hydrated lime, and quicklime. Lime in a slurry form is used most frequently. A system similar to that shown in Figure 3 is needed for plants which use quicklime.

Neutralization with lime requires the preparation of the lime slurry by “slaking” quicklime. The following chemical reaction occurs:

\[
\text{CaO + H}_2\text{O} \rightarrow \text{Ca(OH)}_2
\]

“quicklime” “hydrated lime”

The calcium hydroxide is then mixed with the pickle liquor. The lime slurry is fed at an excess of 15 to 35 percent above the theoretical rate to assure complete neutralization.

Neutralization of spent pickle liquor requires two reactions. The free sulfuric acid is neutralized by the calcium hydroxide:

\[
\text{H}_2\text{SO}_4 + \text{Ca(OH)}_2 \rightarrow \text{CaSO}_4 + 2\text{H}_2\text{O}
\]

and the ferrous sulfate is changed to ferrous hydroxide by the calcium hydroxide:

\[
\text{FeSO}_4 + \text{Ca(OH)}_2 \rightarrow \text{CaSO}_4 + \text{Fe(OH)}_2
\]

Thus, the lime requirements are greater than those for neutralizing only the acid.

After the acid is neutralized, the precipitated calcium sulfate and iron hydroxide must be separated from the liquid.

Separation of the finely divided solids from the liquid is difficult, since ferrous hydroxide does not settle easily. Therefore, obtaining an overflow of sufficient clarity to discharge to a stream often is a problem.\(^1\) If the sludge is to be transported a long distance for disposal, the additional water may be removed by vacuum filtration. In many cases, the neutralized stream is pumped directly into a lagoon which has a large holdup time (several days), which allows the separation of the liquid and solids.

Combined Neutralization and Oxidation

To overcome the difficulty in separating the ferrous hydroxide, a modified neutralization technique which includes neutralization of the spent pickle liquor plus oxidation of the ferrous hydroxide to magnetite ($\text{Fe}_3\text{O}_4$) has been developed. Magnetite settles much more readily than ferrous hydroxide. This system also offers the possibility of recovering magnetite as a by-product. The investment for this process is significantly higher than that for simple neutralization. A discussion of this process is outside of the scope of this report.

Contract Disposal

Many companies contract with other firms for hauling and disposal of their spent pickle liquor. No pickling system changes or investment for treatment facilities are required. However, depending upon the specific situation, contract hauling can be expensive because of transportation costs. It is impractical for handling rinse waters. The conditions when contract disposal is economical are discussed in Section 4.

\(^1\) If the plant is discharging to a municipal system, this may not be critical.
Figure 3: Complete Neutralization System

- Lime Injection Tank
- Lime Storage
- Rinse Water and spent process liquors
- Equalization Tank
- Two-stage Neutralization
- Overflow to Manual pH Stabilizer
- To Dense Sludge for Disposal or Dewatering
- Polymer Storage
- Control System
COMPARING THE OPTIONS

The use of an acid recovery system offers the manufacturer a savings in acid costs and greatly reduces his pollution control problems. Neutralization not only does not recover the acid in the pickle liquor, but it requires the manufacturer to purchase lime for its neutralization. On the other hand, the original investment for a neutralization system can be less than that for acid recovery under certain conditions, and the installation of neutralization technology normally does not require many modifications in the manufacturing area. Contract disposal of spent pickle liquor offers minimization of investment at the possible price of high operating costs. The relative advantages of each of these factors must be evaluated before a wise decision can be made for any specific facility. This section contains information which will allow the manufacturer to evaluate the performance and economics of these options under the operating conditions at his plant. To arrive at this data, the manufacturer needs to know only the percentage of iron and free acid in the pickle liquor when it is considered “spent,” and the percentage of steel loss in pickling.

If the pickling iron loss is not known, it can be estimated by averaging the iron and sulfuric acid composition in the spent pickle liquor over a period of time and using the following formula:

\[
\% \text{Iron} = \frac{\text{Tons of } 100\% \text{H}_2\text{SO}_4 \text{used}}{\text{Loss} \cdot \text{Tons of Steel Pickled/yr} \times (1.75 + \frac{\% \text{Free H}_2\text{SO}_4 \text{in spent liquor}}{\% \text{Fe in spent liquor}})}
\]

This formula neglects the iron lost in the rinse water.

Purchased Materials

The acid recovery system requires no lime and reduces acid requirements. If the wastewater flow is reduced so that all the pickling solution and rinse waters pass through the acid recovery system (i.e., no free acid is lost in the rinse water), the makeup sulfuric acid requirements can be estimated from Figure 4 if one knows the amount of iron loss through pickling. The amount of ferrous sulfate crystals produced also can be estimated from this figure.

For example, at an average iron loss during pickling of 0.5 percent, 18 pounds of sulfuric acid will be required per ton of steel. From this same figure it can be determined that 50 pounds of ferrous sulfate heptahydrate crystals will be produced per ton of steel pickled.

The sulfuric acid required to pickle a ton of steel, when hauling or neutralization is used, is a function of the free sulfuric acid and the iron remaining in the spent pickle liquor, as well as the percent of iron loss during pickling. The sulfuric acid makeup requirements can be determined from Figure 5. The quicklime required for neutralization also can be determined from this figure. Figure 5 was prepared on the basis of 1 percent iron loss during pickling. The required acid or lime at any other pickling loss can be calculated by multiplying the value at 1 percent loss by the ratio of the actual iron loss to 1 percent. For example, if a plant considering neutralization is currently dumping its pickle liquor when free acid is at 6 percent and the iron content is at 8 percent, Figure 5 shows that 50 pounds of sulfuric acid makeup will be required per ton of steel pickled, and 38 pounds of lime will be required for neutralization if the iron loss is 1 percent. If the iron loss is 0.5 percent, then 25 pounds of 100 percent sulfuric acid and 19 pounds of lime are needed per ton of steel.

Similarly, the calcium and iron hydroxide sludge produced by the neutralization process can be determined from Figure 6.

Figure 7 shows the amount of pickle liquor produced as a function of iron loss and pickle liquor composition.

Using these figures, Table 1 was constructed for a 100,000 TPY wire plant under the stated conditions.

Economics

Variabilities in operating conditions and in the availability of land among pickling facilities must be considered in evaluating the economics of each process. In this section the major factors which may affect the economics are discussed, and detailed costs are presented for a typical case so that each manufacturer may evaluate the best choice for his particular situation.
Figure A:
Sulfuric Acid Makeup Requirements for Pickling and Ferrous Sulfate Crystals
Produced with Acid Recovery

Read left for sulfuric acid
Read right for ferrous sulfate crystals produced
Figure 5.
Sulfuric Acid and Lime Requirements for Neutralization of Pickle Liquor and Rinse Water for 1% Iron Loss

To obtain lbs. of hydrated lime multiply x 1.32

Figure 6.
Sludge Production from Neutralization of Spent Pickle Liquor for 1% Iron Loss

NOTE:
The graph gives dry solids. To correct for water contained in the sludge, multiply by the following factors:

<table>
<thead>
<tr>
<th>Solids</th>
<th>Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0.43</td>
</tr>
<tr>
<td>50</td>
<td>0.67</td>
</tr>
<tr>
<td>70</td>
<td>1.00</td>
</tr>
<tr>
<td>90</td>
<td>1.50</td>
</tr>
<tr>
<td>120</td>
<td>3.33</td>
</tr>
<tr>
<td>150</td>
<td>6.00</td>
</tr>
<tr>
<td>180</td>
<td>10.00</td>
</tr>
</tbody>
</table>

The expected % solids for various solid/liquid separating devices can be obtained from laboratory, settling tanks, or vendors. A 50% solids value might be used as a basis for initial estimating. This value must be confirmed before reaching a final decision.
Figure 7.
Spent Pickle Liquor Volume/Ton Steel Pickled
for Hauling and Neutralization

Pickle Liquor Generated (gallons/ton of steel)

1.5% Fe Loss

1.0% Fe Loss

0.5% Fe Loss

Rinse Water is Not Included
Density @ 10 lb/gal
Curves apply for all H₂SO₄ levels in spent liquor

% Dissolved Iron in Spent Liquor
<table>
<thead>
<tr>
<th></th>
<th>Case I: 0.5% Iron Loss</th>
<th>Case II: 1.0% Iron Loss</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Acid Recovery</td>
<td>Neutralization</td>
</tr>
<tr>
<td>Total Iron Loss</td>
<td>500</td>
<td>500</td>
</tr>
<tr>
<td></td>
<td>(tons/year)</td>
<td>(tons/year)</td>
</tr>
<tr>
<td>Sulfuric Acid Makeup</td>
<td>300</td>
<td>1400</td>
</tr>
<tr>
<td></td>
<td>(tons/year)</td>
<td>(tons/year)</td>
</tr>
<tr>
<td>Quicklime Required</td>
<td>0</td>
<td>1075</td>
</tr>
<tr>
<td></td>
<td>(tons CaO/year)</td>
<td>(tons CaO/year)</td>
</tr>
<tr>
<td>Spent Liquor Composition (weight %)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Unreacted H₂SO₄</td>
<td>3</td>
<td>8</td>
</tr>
<tr>
<td>Plant Wastes and By-products</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crystalline Fe₂O₄ &amp; H₂O</td>
<td>2820</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>(10% Moist.) (tons/year)</td>
<td>(tons/year)</td>
</tr>
<tr>
<td>Sludge at 20% Average Solids</td>
<td>0</td>
<td>15700</td>
</tr>
<tr>
<td></td>
<td>(tons/year)</td>
<td>(tons/year)</td>
</tr>
<tr>
<td>Wastewater (gallons/hr)</td>
<td>0</td>
<td>35000</td>
</tr>
</tbody>
</table>

Assume 1 gal = 3.785 liters. Water per ton of steel, and 250 operating hrs per year.
Investment for Acid Recovery

The investment required for installing an acid recovery system falls into three distinct categories:

1. The acid recovery equipment.
2. Modifications to existing pickling and rinse tanks to reduce water flow--these changes bring the water balance to the point where zero discharge is achieved.
3. The installation of an improved air exhaust and demisting system--this system greatly improves the operating environment around the pickling line, and it is optional for each plant.

It is important to note that part of the investment required for acid recovery results in a direct improvement of the pickling operation. Staged rinsing, for example, reduces the water usage of the plant. Air agitation may improve pickling rates. The air exhaust system vastly improves the plant environment by controlling acid fumes and, therefore, can be at least partially chargeable as an air pollution control investment.

The investment for acid recovery, as shown in Figure 8, assumes an iron and sulfuric acid concentration in the spent pickle liquor of about 8 percent. Neutralization investment costs are a strong function of the spent pickle liquor composition and volume because these values set the size of the lime slaking system as well as that of the neutralization vessels. The amount of rinse water also is a critical value and directly affects the size of the neutralization vessels. Unlike the investment shown for acid recovery, the neutralization costs do not include any investment for modifications of the rinse system. Therefore, the installed investment for neutralization is shown for two rinse water rates. The installed investment includes equipment for neutralization of the pickle liquor and rinse water and provides for a clarifier and thickener to concentrate the neutralized sludge. It is assumed that the concentrated solids leave the thickener containing about 20 percent solids. Costs for further solids concentration equipment, such as vacuum filters or centrifuges, are not included. No in-plant modifications or land costs are included.

The neutralization investment costs were derived from a recently completed comprehensive study by EPA on the costs required to maintain the pH of strong acid wastes between six and nine almost all of the time.

Because of the minimum practical size for lime slaking and the necessity for a basic control system regardless of size, the investment costs for a continuous system do not decrease significantly for very small plants. Plants with small flows should investigate batch neutralization, which may decrease the investment requirements.

The investment for contract hauling is too dependent upon local conditions for inclusion in this report. However, depending upon the contractor’s schedule, some storage and pumping capacity will be required. Neutralization facilities for rinse water also will be required.

Operating Costs

Operating costs are a function of the following factors:
- Raw material and utility consumption;
- Iron loss to the pickling solution;
- Spent pickle liquor composition;
- Volume of rinse waters.

The annual operating costs for acid recovery and neutralization are presented in Figure 9. Figure 10 shows the operating costs per ton of steel pickled. Table 2 lists all of the major assumptions related to Figure 9.

The acid recovery operating costs bracket the most likely conditions. In one case, sulfuric acid is valued at $25/ton (including freight) and a net loss of $10/ton is taken for ferrous sulfate crystals. In the second case, sulfuric acid is valued at $50/ton and a $5/ton credit is taken for ferrous sulfate crystals.

Neutralization costs are very sensitive to the method of sludge disposal and are shown for two conditions:

1. Sludge is disposed of at $3.50/ton. This would allow about a 5-mile haul for sludge containing 20 percent solids.
2. Sludge is disposed of on-site at a negligible cost.
Figure 8.
Investment for Handling Spent Pickle Liquor at 1% Iron Loss

NOTE:
These investment figures are based upon a 1% iron loss and a composition of 8% iron and 8% sulfuric acid in the spent pickle liquor. This figure can be used with somewhat less accuracy for plants which have other percentage iron losses by using the lower scale.

Figure 9.
Annual Operating Costs for Handling Spent Pickle Liquor

- Contract disposal @ $0.15/gallon
- Neutralization with 20% solids, sludge hauled @ $3.50/ton
- Contract disposal @ $0.07/gallon
- Neutralization with on-site disposal of sludge
- Acid recovery with sulfuric acid @ $2.50/ton and a $10/ton disposal cost for ferrous sulfate
- Acid recovery with sulfuric acid @ $50/ton and a $5/ton credit for ferrous sulfate
### Table 2
Economic Cost Base - Pickling Operation with spent Liquor Treatment

<table>
<thead>
<tr>
<th>OPERATING LABOR</th>
<th>Acid Recovery</th>
<th>Neutralization</th>
<th>Hauling</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Man hours/day)</td>
<td>(Man hours/day)</td>
<td>(Man hours/day)</td>
</tr>
<tr>
<td>Pickling Volume to 100,000 tons/year</td>
<td>3</td>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>foreman, operators</td>
<td>90</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>Pickling Volume above 100,000 tons/year</td>
<td>10</td>
<td>15</td>
<td>8</td>
</tr>
<tr>
<td>foreman, operators</td>
<td>7.6</td>
<td>4</td>
<td>0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>UTILITIES/TON STEEL PICKLED</th>
<th>Steam</th>
<th>Water</th>
<th>Electricity</th>
</tr>
</thead>
<tbody>
<tr>
<td>(lb/ton)</td>
<td>(gal/ton)</td>
<td>(kW-h/ton)</td>
<td></td>
</tr>
<tr>
<td>Acid Recovery - Zero Discharge</td>
<td>164</td>
<td>245</td>
<td>5.9</td>
</tr>
<tr>
<td>@ 0.5% Fe Loss</td>
<td>142</td>
<td>270</td>
<td>9.6</td>
</tr>
<tr>
<td>@ 1.0% Fe Loss</td>
<td>132</td>
<td>295</td>
<td>13.1</td>
</tr>
<tr>
<td>Neutralization</td>
<td>17</td>
<td>-</td>
<td>2.4</td>
</tr>
<tr>
<td>Contract Hauling</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

### COST BASIS

- **Operating Labor**: $12,500 per man-year
- **Foremen**: $15,000 per man-year
- **Steam**: 24,500 gal
- **Water**: 13,200 gal
- **Electricity**: 29.5 kw/h
- **Sulfuric Acid**: 10 lb/ton
- **Quicklime**: CaO: 332 lb/ton
- **Solids Shipping Costs**: $5/ton for crystals
- **Neutralized Sludge Hauling Fee**: $25/ton
- **Pickle Liquor Hauling Fee**: $0.14/gal
- **pH Adjustment**: $25,000 for 1,000 gal of lime water
- **Sewer Fees**: $50.40/month
- **Maintenance**: 5% of investment
- **General Plant Overhead**: 1.25% of operating cost
- **Depreciation**: 10% of investment
- **Taxes and Insurance**: 0.5% of investment
- **Maintenance Labor**: @ 37% of maintenance cost

This table represents a baseline rate for pickling operations that can be adjusted for water usage, lime modifications, and other factors. It is a guide to help in planning and estimating costs for pickling operations. Every step of the process has been analyzed to achieve a balanced cost without overcharging the customer or understating the requirements.
For comparison, costs for contract disposal under specific conditions also are shown. More specific costs for contract disposal should be determined by using the amount of pickle liquor shown in Figure 7 in combination with a quote from a contract disposal firm.

It is important to note that it is prohibitively expensive to handle rinse water by contract hauling, and a method for eliminating these wastes still must be found if contract disposal is used. These wastes can be handled by municipal systems after pH adjustment to a range of six to nine. The cost of placing the rinse waters into the proper condition for acceptance by a municipality has been taken at $2.50/1,000 gallons, and a municipal charge of $0.40/1000 gallons has been included in Figure 9. This would allow only very simple in-line neutralization, with minimal solids/liquid separation. Depending upon the strength of the rinse waters, this may be acceptable for some municipal systems. Each manufacturer must check this for his site.

The more optimistic case for contract disposal of pickle liquor $0.07/gallon would allow about a 25-mile haul if there were no other disposal costs. This would be realistic for the cases where a municipal system would be using the spent pickle liquor as a coagulant. In the past, contract haulers had more latitude for disposal of spent pickle liquor than at present. The less optimistic ($0.14/gallon) case presumes there is some charge for disposal after hauling. Contract disposal costs are specific to each site and the manufacturer must independently evaluate this option.

It should be mentioned that the use of a contract hauler places the manufacturer in the position of complete dependence on the contractor for continued operation. The disposal contract should be carefully written.

Table 3 gives a complete economic analysis of all three options for one mill pickling 100,000 TPY of steel. Rinse water disposal requirements were taken at 250 gallons per ton of steel for neutralization and contract hauling. For acid recovery, complete recovery of rinse water and zero discharge were assumed.
Table 3
Comparison of Economics for a
Plant Pickling 100,000 TPY of Steel

<table>
<thead>
<tr>
<th>Item</th>
<th>Basis</th>
<th>Acid Recovery</th>
<th>Neutralization</th>
<th>Contract Hauling</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>BASIS:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1% iron loss; spent pickle liquor composition</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8% dissolved iron, 8% H₂SO₄ all figures in thousands of dollars per year (1976 base)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Item</th>
<th>Basis</th>
<th>Acid Recovery</th>
<th>Neutralization</th>
<th>Contract Hauling</th>
</tr>
</thead>
<tbody>
<tr>
<td>Investment Salaries</td>
<td>Figure</td>
<td>630.0</td>
<td>770.0</td>
<td>0</td>
</tr>
<tr>
<td>&amp; Wages</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Operators</td>
<td>$12,500/man year</td>
<td>12.5</td>
<td>12.5</td>
<td>6.2</td>
</tr>
<tr>
<td>Foremen</td>
<td>$15,500/man year</td>
<td>1.5</td>
<td>3.8</td>
<td>0</td>
</tr>
<tr>
<td>Utilities</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steam</td>
<td>$2.50/1000 lbs.</td>
<td>35.4</td>
<td>4.2</td>
<td>—</td>
</tr>
<tr>
<td>Process Water</td>
<td>$0.30/1000 gallons</td>
<td>(8.1)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Electricity</td>
<td>$0.02/kW-h</td>
<td>19.0</td>
<td>4.0</td>
<td>—</td>
</tr>
<tr>
<td>Raw Materials</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>$50.00/ton</td>
<td>(50.0)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>CaO</td>
<td>$32.00/ton</td>
<td>0</td>
<td>68.7</td>
<td>0</td>
</tr>
<tr>
<td>Shipping &amp; Hauling Costs</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crystals</td>
<td>$5.00/ton FeSO₄ • 7H₂O</td>
<td>28.8</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Sludge</td>
<td>$3.50/ton</td>
<td>0</td>
<td>110.0</td>
<td>0</td>
</tr>
<tr>
<td>Pickle Liquor</td>
<td>$0.14/gallon</td>
<td>0</td>
<td>0</td>
<td>350.0</td>
</tr>
<tr>
<td>Maintenance</td>
<td>6% of investment</td>
<td>37.8</td>
<td>46.2</td>
<td>—</td>
</tr>
<tr>
<td>General Plant Overhead</td>
<td>1.25 (wages &amp; salaries + maintenance labor)</td>
<td>35.0</td>
<td>41.7</td>
<td>7.8</td>
</tr>
<tr>
<td>Waste Water Costs</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sewer Fees</td>
<td>$0.40/1000 gallons</td>
<td>0</td>
<td>9.2</td>
<td>10.0</td>
</tr>
<tr>
<td>pH Adjustment</td>
<td>$2.50/1000 gallon rinse water</td>
<td>0</td>
<td>—</td>
<td>62.5</td>
</tr>
<tr>
<td>Taxes and Insurance</td>
<td>0.5% of investment</td>
<td>3.2</td>
<td>3.9</td>
<td>0</td>
</tr>
<tr>
<td>Depreciation</td>
<td>10% of investment</td>
<td>63.0</td>
<td>77.0</td>
<td>0</td>
</tr>
<tr>
<td>By-Product Credit</td>
<td>$10.00/ton FeSO₄ • 7H₂O</td>
<td>(52.0)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Total Annual Costs</td>
<td>126.1</td>
<td>381.2</td>
<td>436.5</td>
<td></td>
</tr>
</tbody>
</table>

Rinse Water included in process water for acid recovery plants at 25 gal/ton pickled steel.
*Maintenance labor at 37% of maintenance cost.
Since the acid recovery process is the only treatment unit which produces a by-product for sale or disposal, the operating expenses will vary with the costs or credits associated with that product—ferrous sulfate heptahydrate.

Most existing acid recovery plants now receive a net credit of $8 to $15 per ton of heptahydrate. The widespread use of acid recovery may change this situation. If complete drying and bagging facilities were installed, the crystal value would increase to $35 to $45 per ton, shipped in 50-pound bags. The economics usually are not favorable for installing these extra facilities since the crystal volume is low and drying and marketing expenses are high. Shipping costs for the crystals can be high. Therefore, the net return or loss is a function of the market and the location of the customers.

The effect of changes in the net value of the by-product credit on the total operating cost is tabulated in Table 4.

Because of the varying unit costs and operating conditions, the operating costs for each individual plant may differ greatly from those presented here. By using the correction factors and costs in this report, each manufacturer can compare his costs with those listed, and make the appropriate revisions.

The use of the data in this report to prepare Table 3 is illustrated under the “Example Calculation” (Table 5).

Although each company must evaluate the economics for its specific plant, some general comments can be made:

- At pickling capacities above 75,000 TPY, the acid recovery process appears to be the most economical choice unless a special disposal situation is present, or conditions are such that the existing pickling line cannot be modified to minimize the rinse water produced.
- For capacities below 50,000 TPY, special site conditions will determine the most economical choice.
- Neutralization appears to be economical only for special cases where ample land is available to impound the neutralized pickle liquor and rinse water, and inexpensive sulfuric acid is available for pickling.
- A most important action which can be taken to reduce investment and operating costs for handling spent pickle liquor is to reduce the iron loss from overpickling and by using steel with minimum scale. This reduces the spent pickle liquor volume to be handled, and applies to acid recovery, neutralization, and contract disposal.

### Table 4

The Effects of Net Value of Crystal By-Product (FeSO₄ • 7H₂O) from Acid Recovery on Total Operating Expense/Ton of Steel Pickled

<table>
<thead>
<tr>
<th>% Iron Loss</th>
<th>0.5</th>
<th>1.0</th>
<th>1.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Net Value of Crystal, $/ton Net Value</td>
<td>Increase (+) or Decrease (−) in Operating Costs (Dollars/ton)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$10/ton Net Value</td>
<td>$0.25</td>
<td>$0.50</td>
<td>$0.75</td>
</tr>
<tr>
<td>$5/ton Net Value</td>
<td>−$0.13</td>
<td>$0.25</td>
<td>$0.30</td>
</tr>
<tr>
<td>$0/ton Net Value</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$10/ton Net Loss</td>
<td>+$0.25</td>
<td>−$0.50</td>
<td>+$0.75</td>
</tr>
</tbody>
</table>

Net Value = Crystal Credit − Shipping Costs
Shipping costs calculated on wet basis assuming 10% moisture
Crystal credit calculated on dry basis as FeSO₄ • 7H₂O
<table>
<thead>
<tr>
<th></th>
<th>Acid Recovery</th>
<th>Neutralization</th>
<th>Contract Hauling</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Investment</td>
<td>From Figure 8</td>
<td>From Figure 8</td>
<td>No investment required</td>
</tr>
<tr>
<td>2. Wages</td>
<td>Man-days from Table 2</td>
<td>Man-days from Table 2</td>
<td>Man-days from Table 2</td>
</tr>
<tr>
<td>3. Steam</td>
<td>142 lb/ton steel from Table 2*</td>
<td>17 lb/ton steel from Table 2</td>
<td>None required</td>
</tr>
<tr>
<td>4. Process Water</td>
<td>270 gal/ton steel*</td>
<td>None charged to pollution control system</td>
<td>None charged to pollution control system</td>
</tr>
<tr>
<td>5. Electricity</td>
<td>9.5 kW-h/ton steel from Table 2*</td>
<td>2.0 kW-h/ton steel from Table 2</td>
<td>None chargeable</td>
</tr>
<tr>
<td>6. H₂SO₄</td>
<td>Reduced consumption, and it is treated as a credit.</td>
<td>None chargeable</td>
<td>None chargeable</td>
</tr>
<tr>
<td>7. CaO</td>
<td>None</td>
<td>428 lb/ton steel from Figure 5</td>
<td>None</td>
</tr>
<tr>
<td>8. FeSO₄·7H₂O</td>
<td>100 lb/ton steel dry basis from Figure 4. At 10% free moisture crystal rate = 111 lb/ton steel (100 + 0.9). Shipping costs at prevailing rate.</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>9. Sludge Hauling</td>
<td>None</td>
<td>626 lb/ton steel (wet basis) from Figure 6</td>
<td>None</td>
</tr>
<tr>
<td>10. Pickle Liquor Hauling</td>
<td>None</td>
<td>None</td>
<td>25 gal/ton of steel from Figure 7. Obtain fees from contractor</td>
</tr>
<tr>
<td>11. Maintenance</td>
<td>At 6% of investment</td>
<td>At 6% of investment</td>
<td>At no charge</td>
</tr>
<tr>
<td>12. General Plant Overhead</td>
<td>At 1.25 (wages + maintenance labor, Maintenance labor at 37% of maintenance cost)</td>
<td>At 1.25 (wages + maintenance labor), Maintenance labor at 37% of maintenance cost</td>
<td>At no charge</td>
</tr>
</tbody>
</table>

*Numbers for 10% from loss
### Table 5 (Continued)
Calculations Derivation for Operating Costs
Based on Examples for Table 3

<table>
<thead>
<tr>
<th>Acid Recovery</th>
<th>Neutralization</th>
<th>Contractor Hauling</th>
</tr>
</thead>
<tbody>
<tr>
<td>13. Sewer Fees</td>
<td>None</td>
<td>Rinse water at 250 gal/ton steel + lime slurry (Fig. 8) + pickle liquor (Fig. 7) less wet sludge (Fig. 6)</td>
</tr>
<tr>
<td>14. pH Adjustment</td>
<td>None</td>
<td>No charge, this is included in neutralization</td>
</tr>
<tr>
<td>15. Taxes and Insurance</td>
<td>At 0.5% of Investment</td>
<td>At 0.5% of Investment</td>
</tr>
<tr>
<td>16. By-product Sales (FeSO₄·7H₂O)</td>
<td>From Figure 4, 711 lb/ton steel</td>
<td>None</td>
</tr>
</tbody>
</table>

*Wire rod before pickling (left), wire rod after pickling and lime coating (right)*
Although the on-site energy requirement for acid recovery systems aimed at zero discharge usually is higher than the requirement for neutralization (depending upon the amount of pickle liquor evaporation required), a comparison of the ultimate energy requirements of the two processes indicates that acid recovery and neutralization energy requirements are about equal at 0.75 percent iron loss and favorable to acid recovery at higher iron losses.

The lime needed for neutralization is manufactured by the calcination of limestone:

\[
\text{CaCO}_3 + \text{Heat} \rightarrow \text{CaO} + \text{CO}_2
\]

The theoretical heat input is approximately 3 million Btu per ton of quicklime (CaO). In actual plant practice, this heat requirement approaches 10 million Btu. Lime rates are, therefore, a very significant portion of the ultimate energy requirements.

Although plants using lime do not directly provide the energy for calcination, eventually they do pay the cost. The cost of lime has risen from $18 per ton in 1972 to $32 per ton in 1976. There is no doubt that future energy cost increases also will be reflected in the price of lime.

Since the amount of pickle liquor used per ton of steel is a function of the iron loss, the ultimate energy consumption for both neutralization and acid recovery also is a function of the same variable. Figure 11 shows the ultimate energy requirements as a function of iron loss for each ton of steel pickled. TPY plant.

Since sulfuric acid is produced by an exothermic reaction, savings in sulfuric acid by acid recovery do not result in large ultimate energy savings.

Figure 11 shows that as the iron losses approach 0.75 percent, the ultimate energy requirements for neutralization and acid recovery are equal at 220,000 Btu/ton of steel. As the iron losses increase, acid recovery is favored. Although the zero discharge acid recovery system requires significant energy for evaporation and refrigeration, neutralization uses large volumes of lime produced from energy intensive processes. Approximately 10 million tons of steel are pickled with sulfuric acid annually and iron losses are usually 1 percent. At this volume, the installation of acid recovery systems achieving zero discharge would increase the national energy usage by 2.4 trillion Btu or the equivalent of 400,000 barrels of fuel oil. The energy usage for neutralization would be about 25 percent higher. This increase in energy usage for acid recovery systems does not take into account the energy savings associated with improving capacities or operation of the plant when operating a closed loop acid recovery system. A decrease in average iron loss per ton of steel would also greatly reduce the energy requirements.

Discharge of ferrous sulfate crystals to storage building

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1 The "ultimate" energy requirement considers the energy to manufacture the required raw materials.
Figure 11.
Ultimate Energy Requirements
Simple Neutralization vs. Acid Recovery
Spent Liquor Composition at 8% Fe and 8% H2SO4

Basis:
Steam = 1000 Btu/lb
Power = 10,000 Btu/kWh
Lime CaO = 9 × 10^6 Btu/lb of lime
Neutralization Utilities
16.5 lbs. steam/ton steel
2.0 kWh/ton
Acid Recovery Utilities
101 lbs. of steam/ton
4.5 kWh/ton @ 0.5% loss
4.5 kWh/ton @ 1.0% loss
11.1 kWh/ton @ 1.5% loss
Pickling tank (foreground), acid mist exhaust system (background)
Dip and spray rinse tank with spray nozzles in operation
Lime coating tank and exhaust system
The Industrial Environmental Research Laboratory in Research Triangle Park, North Carolina, is responsible for control technology in the ferrous metallurgical industry. For environmental information on steel pickling operations and other EPA sponsored programs regarding ferrous metallurgical processes, write:

Metallurgical Process Branch
Industrial Processes Division
Industrial Environmental Research Laboratory
Environmental Protection Agency
Research Triangle Park, N.C. 27711