Use of Spent Pickle Liquor in Waste Treatment

Evaluation for Electroless Copper and Copper Etchant

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Recently, we reported several processes for the treatment of rinse waters containing heavy metal complexes. Other recent publications from the Center describe heavy metal removal technologies which will complement these techniques. Another treatment process developed by Wing and coworkers used ferrous sulfate to remove copper from electroless copper rinse waters. The process gave low residual copper concentrations when alkaline rinse waters were acidified before the addition of ferrous sulfate. Since spent pickle liquors contain ferrous ion and excess acid, these waste solutions were evaluated in the treatment of electroless copper rinse waters.

As part of this study, the spent pickle liquor was also used to treat alkaline copper-ammonia etchant rinse waters.

The "pickling" process is the removal of oxide scale from steel products by immersion in hot dilute sulfuric acid solution. More recently hydrochloric acid has come into use, due to its decreasing price together with its ability to pickle faster, to retain pickling effectiveness at lower acid concentrations, and to be easily regenerated for reuse. Steel is pickled in both batch and continuous equipment. In the case of batch processing, the spent liquor contains between 0.5-2% by wt. free acid and 5.5-8% by wt. ferrous ion (15-22% ferrous sulfate, as FeSO₄). On a continuous pickling operation, spent liquor averages 4-7% free acid and 5.1-5.9% ferrous ion (14-16% as FeSO₄). Spent pickle liquor which, up to the present, has had little commercial value, is produced in the U.S. at the rate of 0.5-1.0 billion gallons annually.

Several methods have been used, or proposed, in the past for disposing spent pickle liquors without treatment. These include discharge into:

1. Deep wells
2. Fissures in cavernous limestone
3. Abandoned mines
4. Exhausted oil and gas sands
5. Artificial lagoons
6. Gravel sumps near large bodies of water
7. Sewers terminating in rivers or lakes

Because of strict EPA regulations, these disposal methods are now limited.

Chemical and Physical Treatment of Pickle Liquors

The treatment of waste pickle liquor is a costly process. Several recent reviews discuss some of the treatments that are used together with operating costs. These treatment methods include:

1. Neutralization
   a. Lime
   b. Magnesium hydroxide
   c. Ammonia
   d. Blast furnace slag or dust
   e. Limestone
2. Crystallization
3. Ion exchange
4. Evaporation
5. Spray tower roasting
6. Vacuum evaporation
7. Electrolytic

The above treatments were developed to utilize the spent pickle liquor as a raw material for producing byproducts which may be recycled in the pickling operation or used in other products. The byproducts and recycled materials include:

1. Ferrous or ferric sulfate in various stages of hydration.
2. Sulfuric or hydrochloric acid values for return to the pickle liquor line.
3. Electrolytic iron plus sulfuric acid.
4. Iron powder.
5. Special grades of iron oxide for pigments plus the return of sulfuric acid values to the pickle line.
6. Iron oxide and ammonium sulfate, the first product being used as a raw material for the open hearth and the latter being used as a fertilizer material.
7. Construction materials.

Some of these processes are becoming more popular because of the cost of other methods of waste treatment.

Waste Treatment Using Pickle Liquor

Frequently, two waste streams can be utilized to provide treatment for each other. Spent pickle liquors for this purpose have been used effectively in some applications.
REDUCTION OF CHROMATE WASTES:

Spent pickle liquor has been used successfully as the reductant for \( Cr^{6+} \) to \( Cr^{3+} \), followed by lime neutralization to precipitate the chromium and iron hydroxides. This reduction occurs most efficiently at pH 2.5-3.0, so the excess acid in the pickle liquor is utilized effectively. The reactions occurring are:

**Reduction**

\[ 2\text{H}^+ + \text{Fe}^{2+} + \text{Cr}^{6+} \rightarrow \text{Fe}^{3+} + \text{Cr}^{3+} + \text{H}_2 \text{O} \]

**Neutralization**

\[ 3\text{Fe}^{2+} + \text{Cr}^{3+} + 12\text{Ca(OH)}_2 \rightarrow 6\text{Fe(OH)}_3 + 2\text{Cr(OH)}_3 + 12\text{CaSO}_4 \]

Since 16 pounds of \( \text{FeSO}_4 \cdot 7\text{H}_2\text{O} \) are required to reduce 1 pound of \( \text{Cr}^{6+} \), the volume of sludge (18 pounds, dry basis) produced after lime neutralization can negate, in some cases, the use of low cost ferrous sulfate pickle liquors.

PHOSPHATE REMOVAL-SLUDGE CONDITIONING:

Spent pickle liquor has been used successfully as a precipitant for phosphates in sewage treatment plants. \(^{1,2} \) Detroit Metropolitan Water Services Department and Milwaukee Sewage Commission have been using the spent liquor for several years. \(^{3,4} \) Treatment plants at Trenton, Mich., and Waukegan, Ill., also have effectively used spent pickle liquor. \(^5 \) The use of the pickle liquor has also been reported to be used as a coagulant and sludge conditioning aid. \(^6 \) The dissolved oxygen or organic content in the municipal flow aids in the effectiveness of the pickle liquor in these treatments. \(^7 \)

Results and Discussion

Samples of spent pickle liquor were obtained from a midwestern steel company. To prevent crystallization of ferrous sulfate, the samples were diluted threefold to yield 1.88% by wt. ferrous ion. The use of 10.6 ml of this pickle liquor would be equivalent to 1.0 g ferrous sulfate heptahydrate.

TREATMENT OF ELECTROLESS COPPER RINSES:

Table 1 shows the results of some of our studies using pickle liquor to remove copper from a quadrol-based electroless copper rinse. The acid present in the pickle liquor was sufficient to lower the pH to 2.5, which weakened the bonds of the complex sufficiently for the \( Cu^{2+} \) to \( Cu^{+} \) reduction to take place. Excellent copper removal was obtained after neutralization to above 11.0 with caustic or lime. Polyelectrolyte flocculation of the precipitated metal hydroxides gave a fast settling floc and a clear supernatant. Residual copper concentrations were always low, and residual iron concentrations low if the pH was adjusted to above 11, as previously reported. \(^8 \)

TREATMENT OF COPPER AMMONIA ETCHANT RINSES:

Ammonium persulfate and alkaline \( [\text{NH}_3\text{Cu/\text{NH}_2\text{OH}} \) or \( (\text{NH}_3)_2\text{CO}_3/\text{NH}_2\text{OH} ) \) etchants are very useful in the printed circuit industry to etch copper from circuit boards. Rinse waters from these etching operations contain the \( \text{Cu(NH)}_2^{++} \) complex, for which most conventional treatments are ineffective. We recently showed that insoluble starch xanthate would effectively remove copper in these rinses.

When pickle liquor was evaluated on these rinses we found that excellent copper removal was obtained. Table 2 shows the amount of pickle liquor (ferrous ion) required and the pH to which the rinse should be adjusted after the pickle liquor treatment, for maximum copper removal. Approximately a three- to fourfold weight excess of ferrous ion is required to remove the copper to below present discharge limits. In all cases the iron content of the final solutions was very low (<0.2 mg/L). When ferrous sulfate was added to copper-ammonia rinses as a solid, in solution, or even pre-acidified with sulfuric acid, low residual copper concentrations were produced but very poor flocculation of the precipitated hydroxides was obtained. Excellent flocculation was always observed in the pickle liquor studies.

Since it is the ferrous ion that is reducing the copper to aid its removal, a sulfuric or hydrochloric acid based pickle liquor can be utilized. The spent pickle liquor can also be used in its concentrated form, but the spent pickle liquor might have to be heated to redissolve any crystallized ferrous sulfate. To treat 1000 gallons of a 50 mg/L copper-quadrol or copper-ammonia rinse, approximately 3 gallons of

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**Table 1. Spent Pickle Liquor Treatment of Quadrol-Based Electroless Copper Plating Rinse Waters**

<table>
<thead>
<tr>
<th>Initial Copper Conc., ( \text{mg/L} )</th>
<th>Initial ( \text{pH} )</th>
<th>Pickle Liquor, ( \text{ml} )</th>
<th>Neutralization Agent</th>
<th>Final ( \text{pH} )</th>
<th>Residual Copper Conc., ( \text{mg/L} )</th>
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<tbody>
<tr>
<td>50</td>
<td>11.2</td>
<td>10.8</td>
<td>( \text{NaOH} )</td>
<td>11.4</td>
<td>0.05</td>
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<tr>
<td>50</td>
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<td>32.0</td>
<td>( \text{NaOH} )</td>
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<td>0.44</td>
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<tr>
<td>500</td>
<td>11.6</td>
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<td>1000</td>
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<td>( \text{NaOH} )</td>
<td>11.4</td>
<td>0.50</td>
</tr>
<tr>
<td>1000</td>
<td>12.0</td>
<td>53.0</td>
<td>( \text{Ca(OH)}_2 )</td>
<td>11.4</td>
<td>0.31</td>
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</table>

* Solutions (1000 ml, 50-1000 mg Cu/L) were treated with the indicated amounts of pickle liquor (18.8 g/L ferrous ion) at pH 2.5 for 15 min. The solutions were neutralized with sodium hydroxide (5N) to the indicated pH and then flocculated with anionic polymer (2.5-5.0 mg/L). The samples were filtered through filter paper for analysis using atomic absorption spectrometry.

**Table 2. Spent Pickle Liquor Treatment of Copper-Ammonia Etchant Waters**

<table>
<thead>
<tr>
<th>Initial Copper Conc., ( \text{mg/L} )</th>
<th>Pickle Liquor, ( \text{ml} )</th>
<th>Final ( \text{pH} )</th>
<th>Residual Copper Conc., ( \text{mg/L} )</th>
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* Solutions (1000 ml, 50 mg Cu/L) were treated with the indicated amounts of pickle liquor (18.8 g/L ferrous ion) at pH 9.4 for 15 min. The solutions were neutralized with sodium hydroxide (5N) to the indicated pH and then flocculated with anionic polymer (2.5 mg/L). The samples were filtered through filter paper for analysis using atomic absorption spectrometry.
spent pickle liquor (6.6% by wt. ferrous ion) would be required.

References