Spent pickle liquors are generated by the steel making and metal finishing industry. Caustic aluminum solutions are generated by aluminum extruding operations. Because of the high metals content of these solutions, disposal is sometimes difficult. The most common disposal alternative for these aluminum and iron salt solutions is on-site treatment consisting of neutralization and precipitation, deep well injection, reprocessing to separate the acid or alkali from the metal and reuse in municipal and industrial wastewater treatment systems. Today, many engineers and scientists are investigating the potential of the last two disposal alternatives. The objective of this paper is to evaluate the potential of reusing spent pickle liquors and caustic aluminum solutions in municipal wastewater treatment systems.

BACKGROUND

Iron and aluminum salts which are derived from virgin materials are commonly used in municipal and industrial waste treatment systems for many purposes. First, iron salts typically in either a ferrous chloride or ferrous sulfate form are injected into sewers to produce a ferrous sulfide precipitate which prevents the evolution of hydrogen sulfide. Secondly, iron and aluminum salts are used to precipitate phosphorus. Usually the precipitation occurs in the primary and/or secondary clarifiers, but can
be accomplished in tertiary clarifiers. Thirdly, iron and aluminum salts added to primary and secondary clarifiers promote coagulation thereby enhancing settling of suspended solid particles. Finally, iron salts are used along with lime to chemically condition wastewater sludge prior to dewatering.

**PICKLE LIQUOR SOURCES AND CHARACTERISTICS**

During the forming and finishing operations, steel products are exposed to the atmosphere, which causes an oxide scale to form on the surfaces. Without a properly cleaned surface, protective coatings will fail to adhere. The most common method for removing the scale is "Acid Pickling", or simply "Pickling". Pickling is the process during which surface oxides (scale) are chemically removed from the surface of the steel product by immersion in a heated acid solution. Pickling can be performed in either a batch or continuous process. The pickling process is performed during both steel making and metal finishing operations.

The pickle liquor used for the study was generated by a steel tire cord manufacturer engaged in metal finishing operations. The production processes for making steel tire cord material consists of heat treatment of the steel rod, heat removal (quenching) of the rod, rinsing the rod with water, and hydrochloric acid pickling prior to the application of the protective coating. The hydrochloric acid pickling operation is performed in a continuous process. The rod is drawn through six tanks of heated acid, with the flow of acid countercurrent to the movement of the rod.
The constant overflow of "spent" pickle liquor is replaced with fresh hydrochloric acid.

An assay was performed on the pickle liquor to determine various metals concentrations, acid content, and other physical characteristics (see Table 1). The iron concentration of the pickle liquor was 9 percent which is typical of iron pickle liquors. The free acid content was 9.6 percent which is also typical of pickle liquors. The pickle liquor had a high lead concentration because it had been drawn through molten lead (i.e., lead quench) prior to pickling. The lead acts as the heat sink after having passed the rod through a high temperature furnace. Residual lead is carried by the rod into the pickling bath and removed by the acid. In processes where no lead quenching is performed, the lead concentration would be much lower. The source of the other metals present in the pickle liquor are from the iron rod.

The caustic aluminum solution is a byproduct of an aluminum extrusion process. The process consists of heating the aluminum billets. The heated aluminum is then extruded through dies into various shapes and configurations. During the process, residual aluminum builds up on the dies. Occasionally, the die is cleaned using a heated solution of concentrated sodium hydroxide. The spent caustic solution contains aluminum at a concentration of two to five percent. Analyses of the waste characteristics of the die burnout solution are presented in Table 1. The
data shows the aluminum concentration to be 18,980 mg/L. The only toxic metals with concentrations detected above 1 ppm were copper, lead, nickel, and zinc. The source of these metals is the aluminum alloy.

**MATERIALS AND METHODS**

Jar tests using a municipal wastewater sample were utilized to evaluate phosphorus removal by precipitation of spent pickle liquor and the caustic aluminum solutions. To establish a baseline for comparison, tests were also performed using ferric chloride. For this study, a two-phase jar test study was performed. In the first phase, the optimum pH for phosphorus precipitation was determined. During the second phase, the relationship between dosages of metal and phosphorus precipitated was determined at the optimum pH.

Wastewater samples were obtained from the R.M. Clayton wastewater treatment plant in Atlanta, Georgia. The sample was taken subsequent to the grit chambers and prior to the primary clarifiers. Samples of spent pickle liquor and die burnout were obtained from a tire cord plant and an aluminum extruding plant, respectively.

Jar testing was performed to simulate a municipal wastewater treatment system. The procedure consisted of rapid mixing of the reagent and the wastewater for one minute followed by slow mixing to promote flocculation for five minutes. The solution was allowed to settle for one hour to simulate primary clarification. Tests for phosphorus, iron, aluminum, and pH were performed on the supernatant.
RESULTS AND DISCUSSION

According to published literature the optimum pH range for phosphorus removal by both ferrous and ferric iron salts is between pH values of 7.0 to 8.0, while removal by aluminum salts is in the range of 5.5 to 6.51, 2. At the optimum pH, the literature shows a phosphorous removal of 70 percent3.

Phase 1 – pH Optimization

Tests were performed using a constant reagent dosage and different pH levels. This was done for each of the three reagents. The dosages for each reagent were chosen at approximately six times the molar ratio of metal (iron or aluminum) to phosphorus. This was done to ensure that complete phosphorus precipitation would occur and only the effect of pH would be tested. A summary of the Phase 1 test results can be found in Table 2.

Figure 1 graphs the relationship between phosphorus removal and pH. It was determined that the optimum pH was 7.0 for both the ferric chloride and the spent pickle liquor solution. For the die burnout solution, the optimum phosphorus removal occurred at a pH between 6.0 and 6.5. The experimental data are in close agreement with the pH ranges of the reported literature. This indicates that no interferences of the phosphorus precipitation process occurred. For the Phase 2 testing, it was concluded that the pH for both the ferric chloride and the spent pickle liquor should be at 7.0. Additionally, in the case of the die burnout solution, the recommended pH was 6.3.
Phase 2 - Dosage Determination and Phosphorus Removal Capacity

After the optimum pH ranges were established, jar tests were performed to determine dosage requirements and phosphorus removal performance for each of the three reagents. In performing the Phase 2 testing, six different dosages were tested. The supernatant was analyzed for orthophosphate (as P), iron and aluminum. Table 3 shows the range of dosages for each reagent and the corresponding phosphorus removal capacity.

The ferric chloride solution achieved a 72% removal efficiency at a molar dosage of 2.1:1 (Fe:P). The stoichiometric ratio to achieve phosphorus precipitation is 1:1. However, dosages greater than stoichiometric are required because iron also precipitates as ferric hydroxide. The data agrees with the reported literature values for primary clarification removal efficiencies. The literature shows molar ratios to range from 1.30:1 to 2.53:1 for a phosphorus removal of 70 percent.

The spent pickle liquor also achieved a 72% phosphorus removal (efficiency) but required a dosage of 5.4:1 (Fe:P). To better understand the need for a higher molar ratio, total iron analyses were performed on the supernatant. From this data, a mass balance on iron and phosphorus was developed. Table 4 shows iron utilized as a function of phosphorus removed. The iron utilized was determined as the difference between the iron added and the iron concentration of the supernatant. Also shown in the table is the ratio of iron utilized to phosphorus removed. At low iron dosages the data shows that iron to phosphorus ratios were in agreement with stoichiometric requirements. One explanation is that the precipitation of the phosphorus did not occur until ferrous ion was
oxidized to ferric ion. Since only a limited amount of oxidation was occurring, total phosphorus removal was not observed. At higher iron dosages, additional phosphorus removal observed may have been the result of a sweep floc or other mechanisms.

The die burnout tests demonstrated that over 90 percent orthophosphate removal could be achieved. Table 3 indicates that phosphorus removal was done at low dosages of aluminum. A removal efficiency of over 90% was achieved at a dosage of 6.6 mg/L as aluminum. This corresponds to a molar ratio of 3.79:1 to 1 (aluminum to phosphorus), however, the stoichiometric molar ratio for precipitation of phosphorus by aluminum is 1:1. The testing data shown in Table 3 indicates over 90% removal at molar ratios of 3.79 to 5.41. This data is in close agreement with reported literature values for the removal of phosphorus in primary clarifiers using aluminum. The literature reports molar ratios of aluminum to phosphorus ranging from 1.39 to 6.69 (Al:P)⁴.

**SUMMARY**

Spent pickle liquor and caustic aluminum solutions were tested to evaluate the potential for phosphorus precipitation. The following conclusions were observed:

1) The optimum pH for phosphorus removal using the iron pickle liquor was approximately 7.0. The optimum pH for phosphorus removal using caustic aluminum solution was approximately 6.3.
2) Phosphorus removal was accomplished using the spent pickle liquor solution. Phosphorus removal efficiency was observed to be 70 percent. The phosphorus removal using the iron pickle liquor required much higher molar dosages than virgin ferric chloride. Analysis of the data showed that most of the ferrous iron remained in solution and did not precipitate readily with phosphorus. It was hypothesized that the precipitation that did occur was caused by oxidation of ferrous ions to ferric ions and the subsequent precipitation as ferric phosphate.

3) Phosphorus removal was precipitated using the spent caustic aluminum solution. The removal percentages measured were greater than 90 percent at molar dosages greater than 3.5 (Al:P).

4) Both spent metal salt solutions were observed to contain heavy metals which may be problematic for use in wastewater treatment systems.
REFERENCES

1 Process Design Manual for Phosphorus Removal. EPA/625/1-7/001, NTIS No. PB-259150, U.S. Environmental Protection Agency, Center for Environmental Research Information. Cincinnati, OH.


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