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Project Summary

Treatment of Metal Finishing Wastes by Use of Ferrous Sulfide

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The demonstration of a new patented sulfide precipitation process ("Sulfex" TN), which removes heavy metals from metal finishing wastewaters, was performed to verify its operational practicability and performance quality. Operational data was also gathered for an economic evaluation of this process.

The study was performed at a carburetor manufacturing plant in Paris, Tennessee. Here, "Udylite" processes are used for chromate conversion coatings on aluminum and zinc carburetor castings before assembly.

A newly installed sulfide precipitation system removes chromium and zinc from the plant's combined metal finishing process wastewater. It also removes suspended material such as precipitated aluminum, iron, and phosphates. Major steps in the system are: equalization and neutralization of untreated wastewater, precipitation of metals and sedimentation of suspended solids, polishing of settler effluent with dual media filtration, and final dewatering of settled sludge.

Results show all metals and suspended solids were removed to levels well below both the City of Paris sewer system limitations and the State of Tennessee guidelines for indirect discharges to sewer systems. A dewatered sludge was produced as a firm, dry cake in a filter press without the use of conditioning agents. No hydrogen sulfide odor was detected from the reaction process treated effluent, or the solid waste produced. Jar tests were demonstrated to be a valuable tool for maintaining good process control and economical operation.

The chemical cost of sulfide precipitation has been found to be directly dependent upon the concentrations of combined zinc and hexavalent chromium present during the sulfide reaction process. Sulfide precipitation was shown to be an economical as well as effective treatment process for this type of wastewater.

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This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

In April 1974, a laboratory and pilot-plant study of a new wastewater treatment process, using sulfide precipitation, was sponsored by the Metal Finisher's Foundation under Grant No.

R802924-01 from the Environmental Protection Agency. In July 1978, another study was undertaken to demonstrate effectiveness, operability, and cost of this new process called "Sulfex"[TN] as a full-scale installation at Holley Carburetor Company in Paris, Tennessee.

Laboratory and Pilot-Plant Study

This work is described in the report "Treatment of Metal Finishing Wastes by Sulfide Precipitation" EPA-600/2-77-049, February 1977.* The project involved precipitating heavy metals normally present in metal finishing wastewaters by a novel process which employs ferrous sulfide addition as well as by conventional treatment using calcium hydroxide for comparison purposes. A simulated metal finishing wastewater containing common heavy metals and chelating agents was used in this laboratory and pilot-plant study. Sulfide precipitation was demonstrated to be a technically viable process that is superior to conventional hydroxide precipitation for removal of copper, cadmium, nickel, chromium, and zinc from the given influent.

Full-Scale Study

The present study was made during the startup of a 7.9 m^3/hr (35 gpm) wastewater treatment system at a carburetor manufacturing plant. Here, the production of carburetors produces wastewater from chromate conversion coating of zinc and aluminum castings by a "Udylite" process. Combined wastewaters from these metal finishing operations contain heavy metal pollutant concentrations in excess of local and state limits set for direct discharge to the city sewer system. Therefore, a safe, reliable, and economic wastewater treatment process was needed by the manufacturer to meet the imposed discharge requirements.

The metal finishing operations used at the plant involved degreasing, deburring, deoxidizing, acid etching, and chromate bath treatment to give carburetor castings corrosion resistant coatings. In the process, various materials including zinc, hexavalent chromium, aluminum, ortho- and polyphosphates, silicates, organic surfactants and chelants, as well as chelated metals, are released into the plant's wastewater discharge.

Since manufacturing specifications vary, all castings do not undergo treatment by each of these finishing operations. Furthermore, the production schedule is quite variable. As a result, the composition of the wastewater fluctuates periodically on hourly, daily and weekly bases.

This type of metal finishing operation is generally used for providing corrosion resistant coatings on surfaces of a wide variety of metal parts, components and appliances. Consequently, these wastewater characteristics are typical of many industrial manufacturing discharges that have to be treated to meet present and future discharge standards.

The laboratory and pilot-plant study had demonstrated the effectiveness of sulfide precipitation on a synthetically prepared metal finishing wastewater. The full-scale system study at the plant is useful in further proving that the process is practical under actual manufacturing conditions. For example, Table 1 summarizes the overall effectiveness of the process in removal of pollutants. Figure 1 shows the total chemical operating cost, on a per shift basis. Other variables and economics are described individually on per shift and per year basis. Therefore, this study shows how practical, controllable, and economical it is to operate the process under the fluctuating contaminant loadings that are characteristic of many metal finishing wastewaters.

Conclusions

Effectiveness

The effectiveness of the sulfide precipitation process has demonstrated that heavy metals can be removed from metal finishing wastewaters to very low levels. The effluent quality produced by this wastewater treatment process (as monitored by direct flame atomic absorption and diphenyl carbazide colorimetric methods for metal analyses) reveals that the process achieves metal values close to or less than are *routinely* detected by the accepted analytical methods (i.e. Cr and Fe detected at 0.05 mg/l, Cu and Zn detected at 0.01 mg/l).

Economics

The chemical cost of the sulfide precipitation process is directly dependent upon the influent metal loading of various heavy metals. At the carburetor plant, influent zinc and hexavalent chromium are the metal concentrations that dictate the dosage of ferrous sulfide that is required. Here, the chemical cost of sulfide precipitation is competitive with the cost of conventional bisulfite and hydroxide treatment for removal of average concentrations of zinc and hexavalent chromium in the untreated wastewater (i.e. about 34 mg/l Zn and 34 mg/l Cr^{+6}).

When hexavalent chromium is present in combination with other heavy metals, as it is at this plant, there can be a savings in equipment cost with sulfide precipitation since the metals can be removed simultaneously in one step. But, as the concentration of zinc (or other heavy metals increases), the chemical cost of direct treatment by sulfide precipitation becomes increas-

Table 1. Average Wastewater Compositions During "Sulfex"[TN] Study

Metal	Untreated* influent	Treated* effluent	Most stringent state or city limit for Paris, Tenn. STP
	(mg/l)	(mg/l)	(mg/l)
Zn	39.5	<0.07†	0.04
Fe	0.52	0.10	—
Cu	<0.01	<0.01	0.5
Cr	32.3	<0.04	1.0
Cr^{+6}	25.6	<0.01	0.05
TSS	46.5	<1.0	<1500

**Average of 22-day test monitoring period (7/11 to 8/11/78).*
†This value is the calculated maximum average for all effluent zinc analysis during this period. As illustrated, elimination of the atypical first sample value (1.5 mg/l Zn) gives an average effluent zinc of less than 0.03 mg/l.

*Schlauch, R.M. and A.C. Epstein. "Treatment of Metal Finishing Wastes by Sulfide Precipitation," EPA-600/2-77-049, Environmental Protection Technology Series, Industrial Environmental Research Laboratory, Cincinnati, Ohio, Feb. 1977, pp. 1-74.

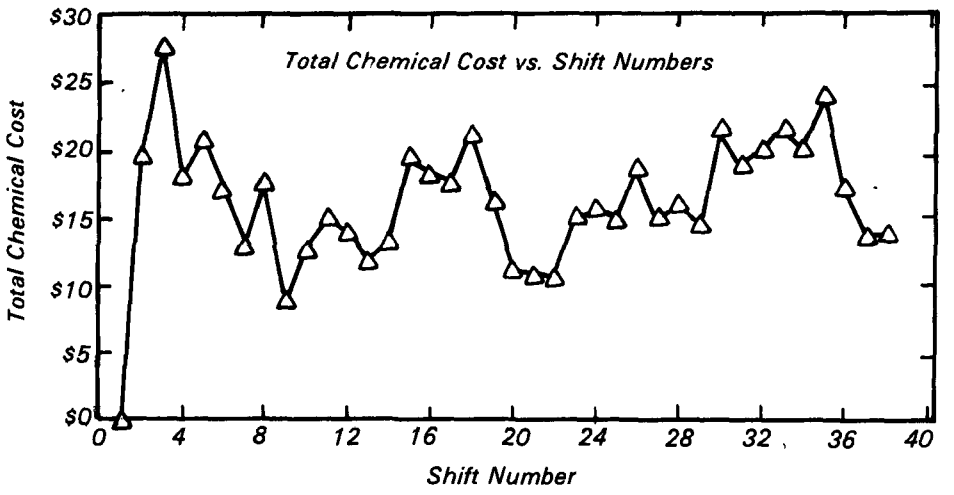

Figure 1. Total chemical cost as a function of time.

ingly more than by hydroxide precipitation. At Holley, the chemical cost for sulfide precipitation treatment is justified since conventional treatment cannot effectively meet the city sewer limitations (i.e. 0.1 mg/l zinc maximum).

In all cases, however, the relative economics can be evaluated beforehand by the average heavy metal concentrations present in the wastewater. In some cases, it may be more economical to remove the bulk of the heavy metals by hydroxide precipitation, and apply sulfide precipitation as a polishing step when stringent criteria must be met.

Most of the basic equipment used for the sulfide precipitation process is the same as would be required for a conventional wastewater treatment process. Therefore, major capital costs as well as operating costs are estimated to be commensurate for both of these treatment processes.

Operation

The operation of the wastewater treatment system at the carburetor plant is basically simple. Good control is maintained because the system is designed to handle sudden changes in wastewater flow and composition.

An equalization tank is an essential part of the system for dampening fluctuations in wastewater flow and metal concentrations into the reactor-settler unit. The concentrated waste sump receives spent metal finishing baths and slowly feeds them into the equalization tank. This sump is essential to minimize variations that could complicate the operation and downgrade the effectiveness of the waste treatment process.

Since it is possible that some residual suspended solids carryover can occur periodically from the settler, the dual-media filter is necessary to ensure removal of suspended metals from the effluent before discharge to the city sewer system.

Without further use of coagulants or conditioners, a filter press will provide excellent dewatering of the settler sludge. A dry sludge cake is produced that releases easily from the press and is ready for disposal.

Control

The pH control of the neutralization process is accomplished in the equalization tank. This type of system is satisfactory for maintaining an appropriate pH for effective metal precipitation in the reactor-settler unit. High concentrations of hexavalent chromium in the wastewater can cause moderate pH increases in the reactor-settler effluent. Controlling the pH at 8.0 in the neutralization step is an effective way of compensating for this pH increase.

Periodic visual jar tests performed on the reactor-settler influent are a satisfactory means of monitoring and controlling optimal ferrous sulfide and polyelectrolyte dosages. These visual tests, for determining chemical dosage requirements, eliminate the need for laboratory analysis of influent heavy metals.

Operating Personnel

The need for wastewater treatment system operators must be determined on the basis of each plant. Due to frequent variation in the mode of the metal finishing operations at the demonstration plant, a full-time operator is required on each shift to monitor the wastewater treatment system. However, in installations where manufacturing processes are not as variable on a daily and weekly basis, a full-time operator may not be required on each shift.

Recommendations

The sulfide precipitation process has demonstrated that more complete metal removal can be obtained and acceptable effluent quality achieved, as opposed to conventional hydroxide treatment of metal finishing wastewaters. But the cost of precipitating most heavy metals (except hexavalent chromium) is higher by sulfide methods than by the hydroxide methods on a per unit weight of metal removed basis.

Present day technology reveals that *hydroxide precipitation* removes high percentages of zinc and other metals from metal finishing wastewaters. However, this removal method can still allow unacceptably high residuals of heavy metals in the treated effluent for discharge.

Therefore, in cases of very high metal loadings, a combination of the two methods in series should prove to be an economically attractive way of achieving superior quality effluents. Sulfide precipitation, is thus precipitation, as a polishing step following conventional hydroxide recommended when either heavy metal loadings on new systems are high enough to warrant the additional equipment or a conventional treatment system already exisits.

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The complete report, entitled "Treatment of Metal Finishing Wastes by Use of Ferrous Sulfide," (Order No. PB 81-233 579; Cost: $9.50, subject to change) will be available only from:
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