United States
Environmental Protection
Agency

Industrial Environmental Research
Laboratory
Cincinnati OH 45268

Research and Development

EPA-600/S2-81-147 Sept. 1981

EPA

Project Summary

Removal of Heavy Metals and Suspended Solids from Battery Wastewaters: Application of HYDROPERM™ Cross-Flow Microfiltration

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Laboratory and full-scale field demonstrations were conducted to demonstrate the applicability of the HYDROPERM™ cross-flow microfiltration system for the removal of suspended solids, and for the removal of suspended toxic heavy metals from lead-acid battery production wastewaters.

The results of the program conducted at Hydronautics, Inc., Laural, Maryland and General Battery Corporation, Hamburg, Pennsylvania show that the system achieves virtually complete removal of suspended solids (the filtrate water has a suspended solids concentration of < 5 ppm) regardless of the feed concentration. Lead is typically reduced to 0.1 ppm.

The waste from the battery manufacturing facility is a mixture of sulfuric acid from occasional dumping of open-tank formation of the anode and cathode battery plates, rinse water from the plate washing facilities, and various floor drains from throughout the plant. The combined total of daily waste production is ~75,000 liters per day (20,000 gallons per day). The waste acid and rinse water mixture is neutralized with high calcium lime to convert the soluble metals to a suspended metal hydroxide form.

The microfiltration system is a treatment process which employs a physical principle of treatment for suspended solids (SS) removal after chemical precipitation. The principal element of the system is a thermoplastic tubular filter (6 mm ID) constructed with a controlled porosity in the micron-size range. Relatively low feed pressures (1.05 kg/cm^2, ~ 15 psi) is employed, which is of significance to energy conservation.

The first phase of the study was to determine the proper porosity, construction material and diameter of the tubes. In addition, studies were conducted to optimize operating conditions (pressure and velocity). The second phase of the study involved the design, fabrication, installation and demonstration of a full-scale system.

Both from a flux and a filtrate quality standpoint, the test and demonstration programs indicated that microfiltration is effective for treating battery manufacturing wastewaters for discharge. Reuse of the permeate is recommended for study.

Microfiltration technology will have wide application in the removal of heavy metals from such industries as battery manufacture, metal finishing, metal refining, and other industries producing similar wastes.

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

Two types of filtration processes have been widely used for removal of suspended solids: (1) the through-flow (e.g., multimedia) filter; and (2) cross-flow filtration (e.g., ultrafiltration and reverse osmosis). Although they can remove some of the suspended solids, conventional through-flow filters have the disadvantage of requiring frequent backwashing, since the filtered particles continuously accumulate on, or actually enter, the filtration barrier. Through-flow filtration is, by its very nature, a batch process, with the flux declining relatively rapidly when the driving pressure differential across the filtration barrier is held constant.

On the other hand, in cross-flow filtration, Figure 1, the direction of the Feed flow is parallel to the filter surface, so that accumulation of the filtered solids on the filter medium can be minimized by the shearing action of the flow. Thus, cross-flow filtration affords the possibility of a quasi-steady state operation with a nearly-constant flux when driving pressure differential is held constant.

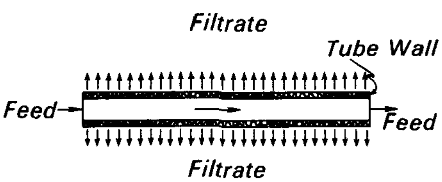

Figure 1. *Cross-flow filtration schematic.*

Cross-flow filtration is intended primarily for the removal of suspended solids and is significantly different from membrance ultrafiltration (UF) or hyperfiltration (RO) which removes substances on the molecular level in addition to suspended solids.

HYDROPERM™ is a thick-walled, porous plastic tube. These tubes, whose wall thickness, inside diameter, porosity, and pore-size distribution can all be closely controlled, can be selected for a particular wastewater so as to obtain optimum performance. The filtration characteristics of the tubes combine both the "in-depth" filtration aspects of multimedia filters and the "surface" filtration aspects of membrane filters. For example, while the removal of micron- and submicron-size particles is often difficult or impossible with conventional gravity settling or through-flow filters, the cross-flow microfiltration tubes are capable of virtually complete removal of such particles.

This report gives a summary of the results of a two-phase program to demonstrate the applicability of the microfiltration system for the removal of toxic heavy metals from lead-acid battery manufacturing wastewaters after the metals have been chemically precipitated. This program was conducted under the sponsorship of the United States Environmental Protection Agency's Industrial Environmental Research Laboratory in Cincinnati, Ohio, under a cooperative agreement to General Battery Corporation, Reading, Pennsylvania. The program was initiated in August 1978 and terminated in June 1980. The results reported in the report include both the Phase I laboratory test program and the Phase II on-site demonstration of a full-scale microfiltration system at the General Battery Corporation plant at Hamburg, Pennsylvania.

The two-phase program is outlined as follows:

The objectives of the Phase I laboratory program were to test, evaluate, and optimize HYDROPERM™ tubes for the effective treatment of battery manufacture wastewaters. Since a unique feature of the tubes is that they can be selected for optimum performance with specific wastewaters by varying the tube material and pore structure as well as the system operating conditions, a principal objective of the proposed program was to conduct such optimization studies.

The objectives of the Phase II program were to design, construct, install, and demonstrate a full-scale microfiltration system at the General Battery Corporation plant in Hamburg, Pennsylvania.

Phase I

The wastewater used for the Phase I laboratory program was obtained from the General Battery Corporation plant at Hamburg, Pennsylvania. The raw wastewaters typically contained ~1500-1900 mg/l of lead. When received at the Hydronautics laboratory, the wastewater had a pH of 1.0. Toxic heavy metals were precipitated at a range of pH's by adding hydrated lime. The best results in terms of lead precipitation were obtained at a pH of 8.5-9.5. After lime addition, total solids (TS) values increased to 45,000 mg/l in the feed, most of which were in the form of suspended solids (SS) (40,000 mg/l).

Thirteen single-tube tests of up to 160 hours in duration were performed with the lime-precipitated waste described above. In all but one of the tests the filtrate was remixed with the feed, which resulted in a "constant concentration" mode of operation. One test was performed with increasing suspended solids concentration in the feed, with periodic removal of the filtrate from the feed until an 85% reduction in the total volume of the feed had been reached. The purpose of these tests was to provide information on filtrate flux and quality as a function of the type of tube and the operating conditions used.

The results of the test program exceeded all original expectations in terms of flux and permeate quality. Forty-hour *plateau* flux levels well in excess of 8150 lmd (200 gal/ft^2-day) were demonstrated in the Phase I laboratory program. These represent *integrated* 40-hour flux values probably in the range of over 12,000 lmd (300 gfd). With periodic cleaning of the tubes, fluxes in the range of 7700-9800 lmd (190-240 gfd) were obtained after a range of 114-164 hours of operation. In addition, when operating at optimum pH (~8.5-9.5) the quality of the permeate was excellent in terms of heavy metals removal. For example, Pb, was typically reduced from > 10 ppm in the feed to as low as < 0.01 ppm in the permeate with median values in the range of 0.6-.09 ppm. Similar results were achieved for other metals, with typical permeate values of: 0.05 for Cu; 0.05 for Ni; < 0.1 for Zn; < 0.002 for As; and ~ 0.3 for Sb. Suspended solids were typically reduced from > 30,000 ppm in the feed (after lime treatment) to less than 10 in the permeate.

Phase II

Figure 2 shows a schematic of the system designed for General Battery, based on the results of Phase I. After the microfiltration system had been installed and interfaced with the system

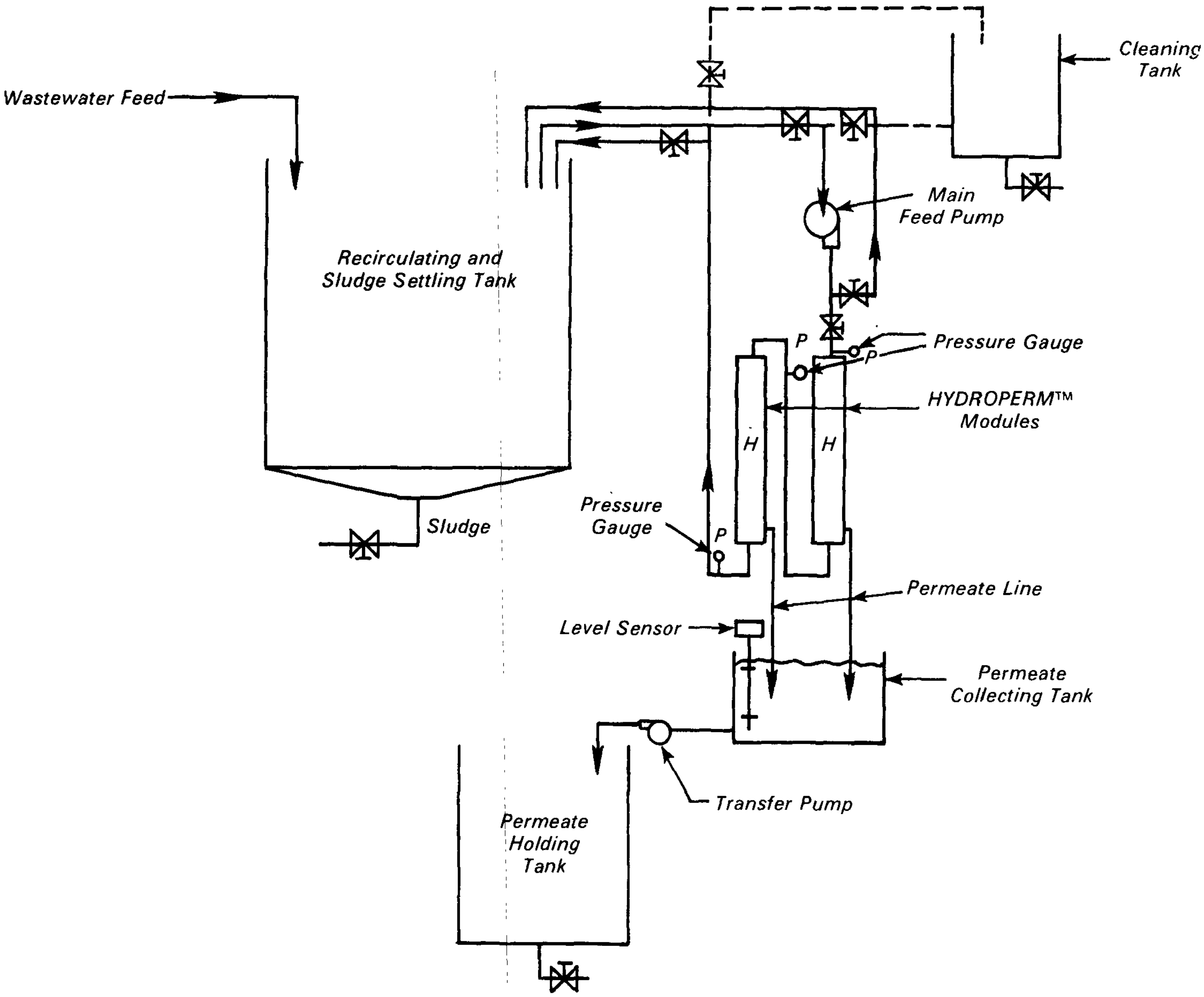

Figure 2. *HYDROPERM™ system schematic diagram.*

components provided by General Battery Corporation, a two-week period of system checkout, debugging, and operator training was initiated. The system checkout included not only the operation of the units but also: (1) definition of the procedure which had to be followed with respect to the plant wastewater neutralization process and (2) preparation of the operational manual based on both the laboratory experience and upon field operation of the unit. Thus, the manual was updated to reflect: field operating conditions; sampling procedures, techniques and frequencies; and the logistics of transporting collected waste feed and permeate samples to and from the independent analytical laboratory. Quick turn-around of laboratory results were critical in terms of the control of the operational procedures to optimize the performance of each individual module.

System Performance in the Field

Permeate Flux and Quality

Initial daily flux values were typically in the range of 32,600 lmd (800 gfd) leveling off to 16,300-20,400 lmd (400-500 gfd) after several hours of operation. The flux was readily restored to the initial value by cleaning the modules for several minutes daily with permeate. Cleaning with dilute HCl (2%) was practiced generally only on a weekly basis.

At these high flux levels, production of permeate by only one unit is in the range of 13,200 to 18,900 liter/hr (3500 to 5000 gal/hr) during a filtration run of several hours duration. Typically, a load of 94,600 liters (25,000 gallons) of wastewater is filtered in 4-1/2 to 5 hours by only one unit, producing 75,700 liters (20,000 gallons) of clear permeate and 18,900 liters (5000 gallons) of sludge. The solids content of the sludge was in the range of 20-35% SS by weight.

Figure 3 shows the frequency of occurrence for lead and suspended solids contents analyzed during the field investigation. It indicates that the majority of the lead concentration in the permeate is below 0.5 ppm. For properly controlled pH adjustment in the neutralization process, lead concentration can be easily reduced to less than 0.2 ppm. This is because most of the toxic metals are amphoteric. They can subsequently precipitate out in the permeate if pH varies which can also contribute to higher suspended solids concentration in the permeate. The suspended solid concentration plot shows that more than two-thirds of permeate samples analyzed have a concentration less than 3 ppm.

Sludge Generation

Waste sludge production is typically about 17,000 liters (4500 gallons) for every two days of operation, with SS concentrations of 20-35% by weight. The wastewater generated at the plant during a typical two-day period is about 94,600 liters (25,000 gallons). From these wastes, approximately 75,700 liters (20,000 gallons) of clear permeate were produced. One tank truck load of sludge is transported to the land-fill site in Reading every other day greatly reduced from the trips which the tank truck had to make in the past (previously, two to three trips were required daily). The clean permeate is discharged directly to a local stream. The reuse of this high quality permeate water for plant use is now under evaluation.

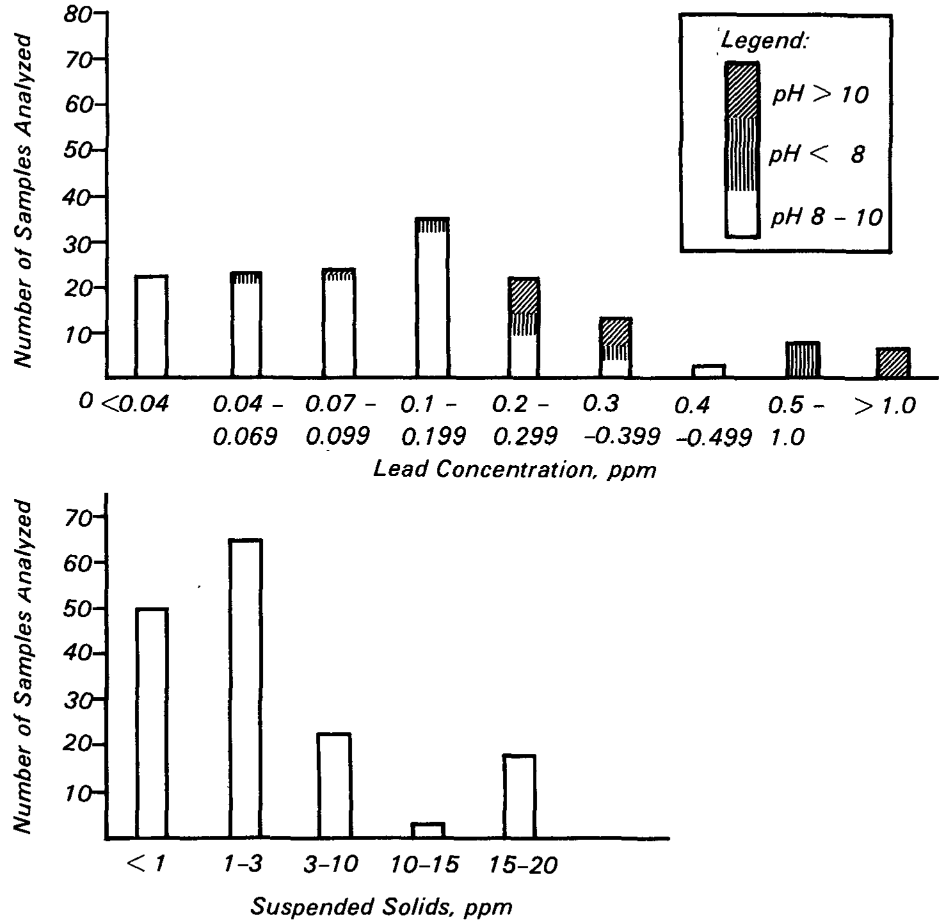

Figure 3. *Pb and SS concentration in HYDROPERM™ permeate from lead-aci battery wastewater.*

Conclusions and Recommendations

General

Cross-flow microfiltration is an effective technology for the treatment of SS in wastewaters from the production of lead-acid batteries.

Permeate Quality

Suspended solids in the feed which exceeded 150,000 ppm were typically reduced to 3 ppm in the permeate. Lead in the feed in the range of several hundred ppm was typically reduced to 0.02-0.1 ppm in the permeate. Other toxic heavy metals, such as Cu, Ni, Zn, As, and Sb were removed with comparable effectiveness. Although the filtrate is discharged directly to a local stream, the quality of the filtrate in terms of SS and toxic heavy metals is such that reuse is also a viable option.

Flux

One HYDROPERM™ unit with 16.7 m^2 (180 ft^2) of filter surface area achieved a plateau flux value of 16,000 lmd (400 gfd), lime-treated, lead-acid battery wastewater.

Sludge

Sludges in the range of 20-35 percent SS by weight were regularly produced by the HYDROPERM™ system.

Recommendations

Cross-flow microfiltration should have broad application for the removal of SS and suspended toxic heavy metals in a wide range of industries, including battery manufacture, metal finishing, smelting and refining, and other industries with similar wastewaters. Economics for the concept remain to be developed.

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***Charles Darvin** is the EPA Project Officer (see below).*

The complete report, entitled "Removal of Heavy Metals and Suspended Solids from Battery Wastewaters: Application of HYDROPERM™ Cross-Flow Microfiltration," (Order No. PB 81-234 833; Cost $9.50, subject to change) will be available only from:

National Technical Information Service
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