



Project Summary

Characterization and Treatment of Aqueous Wastes and Residue from Petroleum Refineries

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This research project was designed to identify process wastewaters which contained a significant proportion of the total load of contaminants in petroleum refinery wastewaters and to evaluate methods for intensively treating these highly concentrated low-volume streams. In addition, selected waste residues from API gravity separator, dissolved air flotation units, and "slop" oil emulsions were analyzed to determine the presence of hazardous chemicals as listed by the U.S. Environmental Protection Agency (EPA) Office of Solid Waste.

Process wastewaters from the fluid catalytic cracking units, crude desalting unit, coking unit, and barometric condenser contained the highest levels of contaminants. These process wastewater streams were major contributors to the total load of phenol, ammonia, sulfide, and organic carbon contamination of the combined refinery wastewaters. On-site evaluations of mixed media filtration-activated carbon adsorption and a biological oxidation system indicated both systems were capable of reducing phenol, sulfide, and organic carbon levels by greater than 90 percent.

This Project Summary was developed by EPA's Robert S. Kerr Environmental Research Laboratory, Ada, OK, 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

The major objective of this project was to determine the relative contribution of aqueous wastes from fluid catalytic cracking (FCC) units and other selected process units to the total quantity of aqueous wastes produced within a refinery. A parallel objective was to evaluate the effectiveness of physical-chemical and biological treatment systems for intensively treating highly concentrated process unit wastewater systems.

Many refineries have adapted a practice of using wastewaters from FCC units for desalting crude oil stocks. This practice reduces concentration of hydrocarbon type compounds in the FCC process wastewater by partitioning hydrocarbons between the aqueous and oily phases. In addition, the total volume of water used is reduced. Most of the refineries are attempting to conserve as much wastewater as possible through recycle-reuse practices. However, complete recycle-reuse may not be economically feasible at this time. As an alternative, existing refineries may have to adopt a combination of recycle-reuse and intensive treatment of highly contaminated process wastewater streams in order to achieve 1983-85 effluent standards.

Phases of Investigation

Phase I (First Year)

Phase I was devoted to characterization of the influent and effluent concentration of aqueous wastes from FCC and other selected process units at three refineries

in Oklahoma and nearby states. The characterization phase was designed to provide quantitative information for determination of the percentage contribution from all other sources within the refinery. Major emphasis was placed on measurement of significant waste components such as organic compounds, ammonia, and sulfides.

Phase II (Second Year)

In the second year of the project, a small, pilot-scale (0.25-gpm) dual media filter-activated carbon treatment system was established to operate in parallel with an existing aerated lagoon (biopond) system which was used to treat wastewaters from a FCC unit. A comparison of the effectiveness of the pilot-scale system with that of the full-sized aerated lagoon system was made by measuring the percent reduction in significant parameters between the influent and effluent streams. The pilot-scale system and the full-sized aerated lagoon system were sampled at six different intervals during a 30-day test period.

Phase III (Third Year)

The objective of this phase of the project was to characterize priority pollutants in residuals from the petroleum refining industry. The residuals were collected from the dissolved air flotation unit, API gravity separator, and "slop" oil residuals. The residuals were extracted by the EPA-RCRA "Extraction Procedure" (EP) for evaluation of solids to determine if they contain toxic substances (CFR 45(98)33127, May 19, 1980) and by conventional laboratory techniques.

Extracts from the residuals were analyzed for toxic heavy metals by atomic absorption spectrometry and for "priority" organic pollutants by combination gas chromatography-mass spectrometry (GC-MS).

Results and Discussion

Phase 1. Collection and Analysis of Contaminants in Process Wastewaters

The concentration of contaminants in the process wastewaters indicated that the overhead contact waters from the FCC unit contained the highest levels of phenol, sulfide, and BOD. The FCC process wastewater stream also contained the second highest level of ammonia. The overhead receiving water from the coking unit contained highest levels of TOC and second highest levels of BOD. The highest levels of oil and grease detected

in a process wastewater stream were from the barometric condenser.

The concentration of mercury, vanadium, cadmium, and nickel was below detection limits for the atomic absorption spectrometer. Detectable quantities of lead were found in process wastewaters from the crude desalting unit and in the combined wastes into the API separator. The caustic neutralizer process wastewaters appeared to be a major contributor of chromium, zinc, copper, iron, potassium, and sodium. Most of the calcium was found in the crude desalting unit wastewaters, although several other waste streams contributed significant quantities of calcium also.

Analyses of specific organic compounds in the process wastewaters by GC-MS indicated that the waste from the caustic neutralizer and the influent to the API separator contained the greatest number of compounds which could be identified. The most common classes of organic compounds identified in the process waste streams were aliphatic (C₁₀H₂₂ to C₂₃H₄₈), monocyclic aromatics, and alkyl aromatics. Only three polynuclear aromatic hydrocarbons were identified — fluorene, phenanthrene/anthracene, and methyl anthracene. These compounds were found in the caustic neutralizer wastewater. None of the aromatic, alkyl aromatic, or polynuclear aromatic compounds were detected in the final effluent, which would indicate that the biological treatment system at this refinery was effectively removing these compounds. The major class of compounds identified in the final effluent was aliphatic hydrocarbons, a homologous series from C₁₃H₂₈ to C₂₀H₄₂.

Phase 2. Comparison of Pilot-Scale Mixed Media Filter-Activated Carbon (MMF-AC) versus Biopond Treatment of Sourwater Stripper Process Wastewater

The calculated mean percentage removal of phenol by the biopond was 99.8% and for the MMF-AC pilot-scale treatment unit 99.99% (Table 1). The mean concentration of phenol in the effluent from the SWS unit was 203 mg/l with a range from 175 to 233 mg/l

in the first on-site evaluation. The mean concentration of phenol in the effluent from the biopond system was 0.269 mg/l with a range from 0.031 to 0.449 mg/l. The mean concentration of phenol in the effluent from the MMF-AC pilot-scale treatment system was 0.002 mg/l with a range from <0.001 to 0.004 mg/l.

The biopond system with the large stabilization basin appeared to be capable of absorbing "shock" loads of high concentrations of organics without malfunction of the biodegradation capacity. Therefore, this system while not capable of achieving the same overall reductions as the MMF-AC during initial stages of the test, would appear to be more reliable for handling the large fluctuations in concentration of waste organics. In addition, the biopond required minimal supervision by refinery personnel.

Ozone Treatment of Sourwater Stripper Effluent

Samples of the sourwater stripper effluent were transported to the laboratory for ozonation. Two tests were performed at high pressure (100 psig) on effluent samples collected September 14, 1981, Run I and Run II. The percent removal of COD was 73% in Run I and 74% in Run II. The percent removal of TOC was not as high, 57% and 56% in Run I and II, respectively, as COD removals. The ratio of COD to TOC decreased from 3.21 at start of run to 2.00 at end. Ammonia concentration was analyzed in Run II to determine if ammonia was creating a chemical oxygen demand. The concentration of ammonia was not significantly altered by ozone treatment.

Two tests were performed at low pressure (8 psig) on effluent samples collected October 8, 1981, Run III and Run IV. The percent removal of COD was 56% in Run III and 57% in Run IV. As in Runs I and II, the percent removal of TOC was less than that for COD, i.e., 35% in Run III and 46% in Run IV. The ratio of COD to TOC was also decreased. Phenol was completely oxidized by the ozone treatment at the end of 4 hours. The phenol concentration was monitored at 1-hour intervals in Run IV and revealed almost complete oxidation of phenol after 2 hours of treatment. No detectable levels

Table 1. Calculated Mean Percent Removal of Contaminants from the SWS Process Wastewaters by the Full-Scale Biopond and the Pilot-Scale MMF-AC Units

	Phenol	Sulfide	Ammonia	BOD	TOC	Oil & Grease
Biopond	99.87	100	24.8	90.1	90.9	95.5
MMF-AC	99.99	100	11.6	95.3	96.9	99.8

of sulfides were found after ozone treatment.

The results clearly indicate ozonation could be used for reduction of COD, phenol, and sulfides in process wastewaters. Ozone treatment for 4 hours was not as effective as activated carbon or the biopond system in percent removal of TOC. Extension of time of treatment would probably improve percent removal of TOC by ozonation.

Based upon comparisons of percent removal of degradable organic contaminants, the pilot-scale MMF-AC and lab-scale ozonation unit could be utilized to treat concentrated process wastewaters from petroleum refineries. The full-sized biopond system at Refinery C achieved equivalent or better efficiencies in removal of COD, TOC, oil and grease, phenol, sulfides and ammonia than the pilot-scale MMF-AC or lab-scale ozonation unit. No attempt was made to estimate capital costs of installation or operation costs of the units evaluated; however, it would appear that the biopond system would be more economical than either of the more advanced types of treatment systems. The MMF-AC or ozone treatment units might be more practical for addition to an existing refinery where space to install a biopond system was not available.

Characterization of Residuals from Petroleum Refining

Residuals from selected process units in four petroleum refineries were analyzed by the EPA Extraction Procedure to determine if these waste products contained sufficient quantities of chemical contaminants to be classified as hazardous materials. The EPA Office of Solid Waste published guidelines defining hazardous materials based upon properties of ignitability, corrosivity, reactivity, and toxicity (*Federal Register* 45:33084-33139, May 19, 1980). If the EP extract of a waste contained concentrations of contaminants in excess of those listed in the *Federal Register*, it would be classified as hazardous and subject to special regulations for transport and disposal.

Five specific waste residuals from petroleum refining were listed as hazardous by the EPA — dissolved air flotation (DAF), slop oil emulsions, heat exchange bundle cleaning sludge, API separator sludge, and tank bottoms from leaded gasoline storage. The following were collected: residuals from API separators at four refineries and samples of slop oil emulsion, dissolved air flotation, bottoms from light oil API separator, solids from a cooling tower blowdown, and sludges from an aerated biopond at three refineries.

The results of the herbicide and chlorinated hydrocarbon pesticide analyses revealed no cases of the petroleum refinery residuals which exceeded EPA criteria. The concentration of mercury in the petroleum refinery residues analyzed was below detection limit.

The EP extracts from the oil refinery residuals were also analyzed for organic contaminants by extraction with methylene chloride at pH <11 and pH <2 to obtain a base-neutral and weak acid fraction, respectively. The base-neutral fraction was then separated into aliphatics, aromatics, and neutral compounds by silica gel chromatography. The aromatic fraction was analyzed by GC-MS to determine specific compounds which might occur in these residues. The number of compounds identified in the aromatic fractions ranged from zero in the cooling tower residues from Refinery C to 42 in the Refinery B slop oil emulsions. The classes of hydrocarbon-type compounds identified ranged from simple monocyclic aromatics such as toluene to complex polynuclear aromatics such as anthracene/phenanthrene. Some compounds containing oxygen and sulfur substitutes were also identified. The alkylated bicyclic and polycyclic aromatic compounds were most abundant in the extracts.

Summary and Conclusions

Phase I

Chemical characterization of selected process wastewaters from petroleum refineries indicated that contact waters from fluid catalytic cracking units, coking units, barometric condensers, and crude desalting units were major contributors of organic contaminants to refinery wastewaters. At Refinery A, where a reasonable estimate of wastewater volumes could be obtained, four process wastewater streams were responsible for greater than 60% of the phenol, sulfide, ammonia, BOD, TOC, and oil and grease contaminants which occurred in the combined wastewaters from the entire refinery. Either elimination of these process contact wastewaters by installation of equivalent non-contact units or intensive treatment of the process wastewaters would improve overall effluent quality from the refineries.

Phase II

The percentage removal efficiency of the full-scale biopond system at Refinery C for conventional pollutant parameters such as phenol, sulfide, BOD, TOC, and oil and grease was greater than 90%. While not as efficient as the pilot-scale

MMF-AC treatment system during initial stages, i.e. greater than 95% removal, the biopond system achieved a better overall removal efficiency than the pilot-scale MMF-AC. The adsorption capacity of the pilot-scale carbon columns for TOC was exceeded by second day during the second on-site test. However, breakthrough of phenol did not occur until the 16th day of the test. The biopond system appeared to be comparable to the MMF-AC system from an overall viewpoint. Laboratory evaluations of the capability of ozonation to reduce organic pollutant loads in concentrated process wastewaters indicated that greater than 73% removal of COD could be achieved within 4 hours of treatment at 100 psig. Low-pressure (8 psig) ozonation achieved greater than 56% removal of COD within 4 hours of treatment. The on-site scale and laboratory evaluations showed that advanced type of treatment systems could be used to reduce total concentration of organic pollutants from highly contaminated process wastewaters. However, these systems would not be as practical or economically feasible as biological oxidation units.

Phase III

Chemical characterization of EP extracts from selected petroleum refinery residuals indicated that the residuals analyzed would not be classified as "toxic" by EPA's criteria. Based upon the results of this project, it would appear that the API separator residuals, and possibly DAF and slop oil emulsions, should not be categorically listed as hazardous wastes but should be analyzed on a case by case basis. Admittedly, the number of petroleum refinery residuals sampled during this project was too few to permit us to determine that these residuals are generally not hazardous. However, sufficient samples were analyzed to determine that not all API separator residuals should be categorically classified as hazardous. The overall results of the three phases of this project clearly indicate the complexity of petroleum refinery wastewaters and residuals. Application of the high resolution capacity of capillary chromatography coupled with the identification capabilities of mass spectrometry resulted in a bewildering list of specific organic contaminants identified in the petroleum refinery process wastewaters. The significance of some of the compounds identified is difficult to ascertain, at this time. Perhaps the most significant finding was the absence of detectable quantities of "priority" pollutants in biologically

treated refinery wastewaters, thus illustrating the effectiveness of biodegradation processes for removal of most of these hazardous organic contaminants or at least reduction of concentrations to non-deleterious levels.

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Leon H. Myers is the EPA Project Officer (see below).

The complete report, entitled "Characterization and Treatment of Aqueous Wastes and Residue from Petroleum Refineries," (Order No. PB 83-260 281;

Cost: \$14.50, subject to change) will be available only from:

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