BIOLOGICAL TREATMENT OF NITRATE BEARING WASTEWATER FROM A URANIUM PRODUCTION PLANT

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ABSTRACT

The Feed Materials Production Center (FMPC) produces uranium metal products used for DOE defense programs resulting in the generation of nitrate- bearing wastewaters. To treat these wastewaters, a two-column fluidized bed biodenitrification facility (BDN) was constructed at the FMPC. The operation of the BDN resulted in substantial compliance with the design criteria limits for nitrate from July through November, 1987. Since the BDN surge lagoon (BSL) proved inadequate for providing nitrate concentration equalization, the BDN feed nitrate concentration fluctuated widely throughout this period of operation. BDN effluent caused a doubling of the hydraulic loading and a tripling of the organic loading on the FMPC sewage treatment plant (STP). Better control of the methanol feed to the BDN, coupled with reduced throughput and improved preaeration, caused a significant improvement in the operation of the STP. The overloading of the STP prompted a decision to add a stand-alone effluent treatment system to the BDN. Preliminary screening tests show that the BDN effluent contains fecal coliforms which will necessitate the disinfection of the final effluent prior to discharge.

BACKGROUND

The Feed Materials Production Center (FMPC) is owned by the United States Department of Energy (DOE) and is managed under contract by Westinghouse Materials Company of Ohio (WMCO). The facility, located near Cincinnati, Ohio, produces uranium metal products used in the fabrication of fuel and target elements for DOE defense programs. A wide variety of chemical and metallurgical processes are utilized at the FMPC. Many of these processes involve the use of nitric acid and result in the generation of nitrate- bearing wastewaters.

Biological denitrification is accomplished by facultative bacteria which, when deprived of free dissolved oxygen (anoxic conditions), utilize nitrate as a final electron acceptor in their metabolism. This metabolism reduces nitrate to nitrogen gas. The overall nitrate removal process is described as:

$$No_3^- + 1.08\ CH_3OH + H^+ =$$

$$0.065\ C_5H_7O_2N + 0.47\ N_2 + 0.76\ CO_2 + 2.44\ H_2O$$

Methanol is utilized as the organic carbon source in this reaction and excess biomass is produced. This biomass is represented by $C_5H_7O_2N$ (1). A two-column fluidized bed biodenitrification facility (BDN) was constructed at the FMPC in 1985 and 1986 to test the feasibility of biological treatment for industrial wastewater streams (Fig. 1). Each column contains anthracite coal particles, 0.25 mm to 0.60 mm in diameter, which provide the surface on which biomass growth occurs. This demonstration facility comprises one-half of the proposed four-column production facility. Process wastewater stored in an 32,176 cubic meters (8.5 million gallon) biodenitrification surge lagoon (BSL) is fed to the BDN.

Methanol is injected and the feed is mixed with effluent from the BDN in order to maintain constant flow. This combined flow is sent to a premix tank where phosphoric acid is added as a nutrient. Next, the flow goes to the #1 feed tank where the pH is adjusted to neutral with sulfuric acid. The neutralized wastewater is then pumped into the bottom of the first BDN column. Nitrogen and carbon dioxide gases, formed from the biological degradation of methanol and nitrate, are vented to the atmosphere. The wastewater overflows the top of the column into the #2 feed tank. Sulfuric acid is again used to neutralize the pH prior to pumping into the bottom of the second column. Wastewater overflowing the second column is processed through one of four vibrating screens which separate anthracite coal from biomass and the treated wastewater. The wastewater is sent to an effluent tank for discharge while the anthracite is returned to the #1 feed tank and pumped back into the first column.

A demonstration test was conducted over a four-month period in 1987. The results indicated the proposed BDN production facility can process FMPC industrial wastewater in a continuous manner while maintaining an effluent that will consistently meet the proposed design parameters for nitrate nitrogen (NO_3-N) and nitrite nitrogen (NO_2-N) (2).

The effluent of the biodenitrification facility averaged approximately three times the levels of five-day biochemical oxygen demand (BOD_5) and total suspended solids (TSS) found in the BDN feed during the demonstration test. Most of the BOD_5 increase was due to inadequate control of the methanol feed concentration.

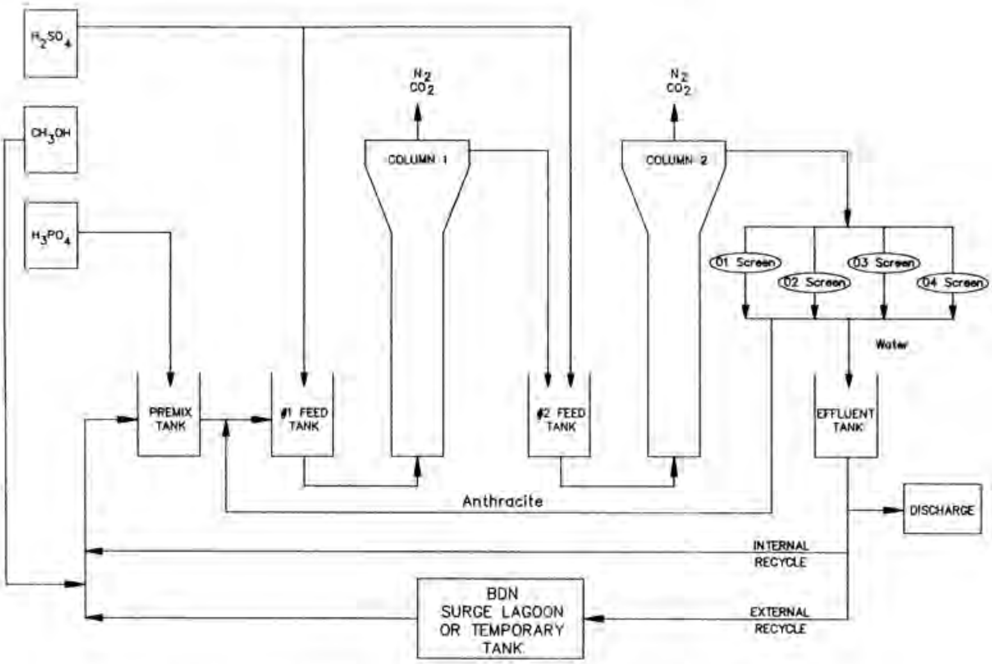

Fig. 1. BDN Demonstration Facility Schematic Flow Diagram.

This paper will discuss the results of continued operation of the BDN from July through November of 1987.

NITRATE REDUCTION

The feed flow to the biodenitrification facility underwent significant changes during the July through November, 1987, period of operation. Figure 2 shows the flow schematic as of November, 1987. Prior to October 1, 1987, the plant process wastewater was routed to the biodenitrification surge lagoon from which it was fed to the BDN.

Due to a repair of the BSL plastic liner scheduled for 1988, two plastic- lined temporary holding tanks were constructed. The 3,785 cubic meter "low" nitrate holding tank, intended to hold the high volume, low (less than 3,000 mg/L NO3-N) nitrate process wastewater, became available for use on October 23, 1987. All process wastewater was diverted to this tank and the BDN operated periodically from this tank. The BDN was fed at a higher rate than process wastewater was fed to the low nitrate tank in order to avoid overfilling the tank, and to allow time to process approximately 15,000 cubic meters of wastewater stored in the BSL. After October 23, and throughout November, the BDN feed alternated between the low nitrate tank and the BSL. The "high" nitrate tank, when activated, will store neutralized raffinate filtrate which is approximately 4% of the total FMPC process wastewater. This wastewater contains 14,000 mg/L of nitrate nitrogen on average and represents 45% of the total nitrate load on the BDN.

The FMPC refinery operation has the largest impact on the amount of nitrate requiring treatment by the BDN. This wastewater is processed in batch fashion at the FMPC General Sump. It is sent to the BSL in relative small volumes (189 cubic meters per batch) but contains very high concentrations of nitrate. The original intent of the BSL was to provide concentration and flow equalization for the mixture of the various process wastewaters including raffinate. Early in the operation of the BDN, it became apparent that the BSL was inadequate for providing concentration equalization. The most plausible explanation is that the BSL inlet and outlet are both near the bottom of the lagoon. Since the neutralized raffinate is more dense than water, it flows from the inlet to the outlet along the bottom of the lagoon in a relatively unmixed manner.

During the BDN demonstration test (2), it was recognized that BDN influent nitrate concentration control would be necessary in order to ensure consistent compliance with nitrate limits without overfeeding methanol into the system. The nitrate concentration continued to fluctuate widely throughout this period of operation (Fig. 3). These fluctuations became even more pronounced when process wastewater was diverted from the BSL to the low nitrate temporary tank.

When hours of refinery operation are directly compared to monthly average nitrate nitrogen concentration in the BSL, no correlation is apparent ($R^2 = 0.056$). However, a correlation is found if lag time is added to reflect the fact that raffinate is not fed to the BDN as soon as it is produced.

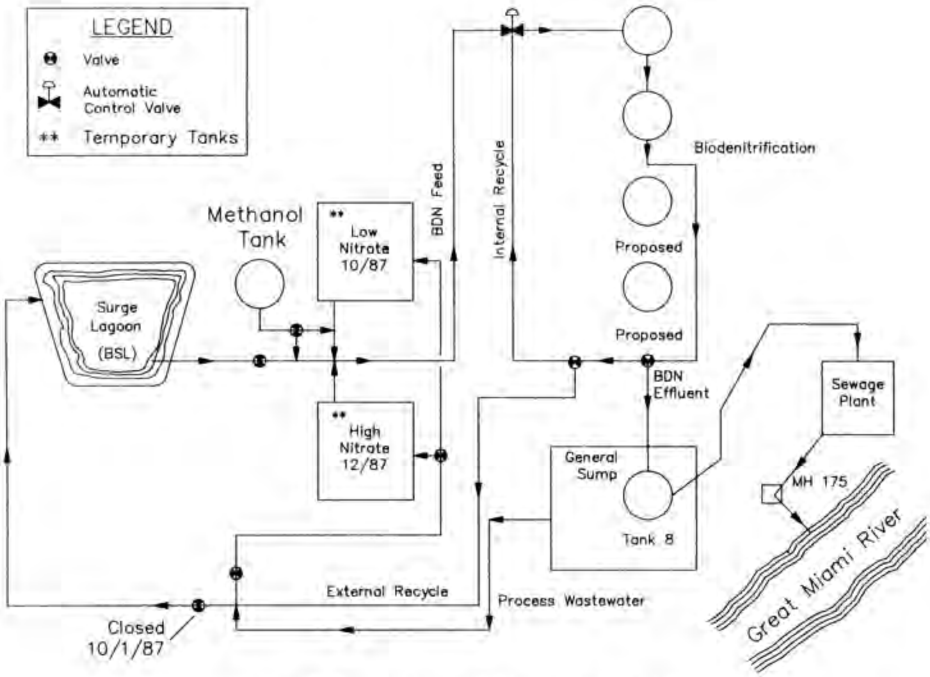

Fig. 2. Flow Diagram November, 1987.

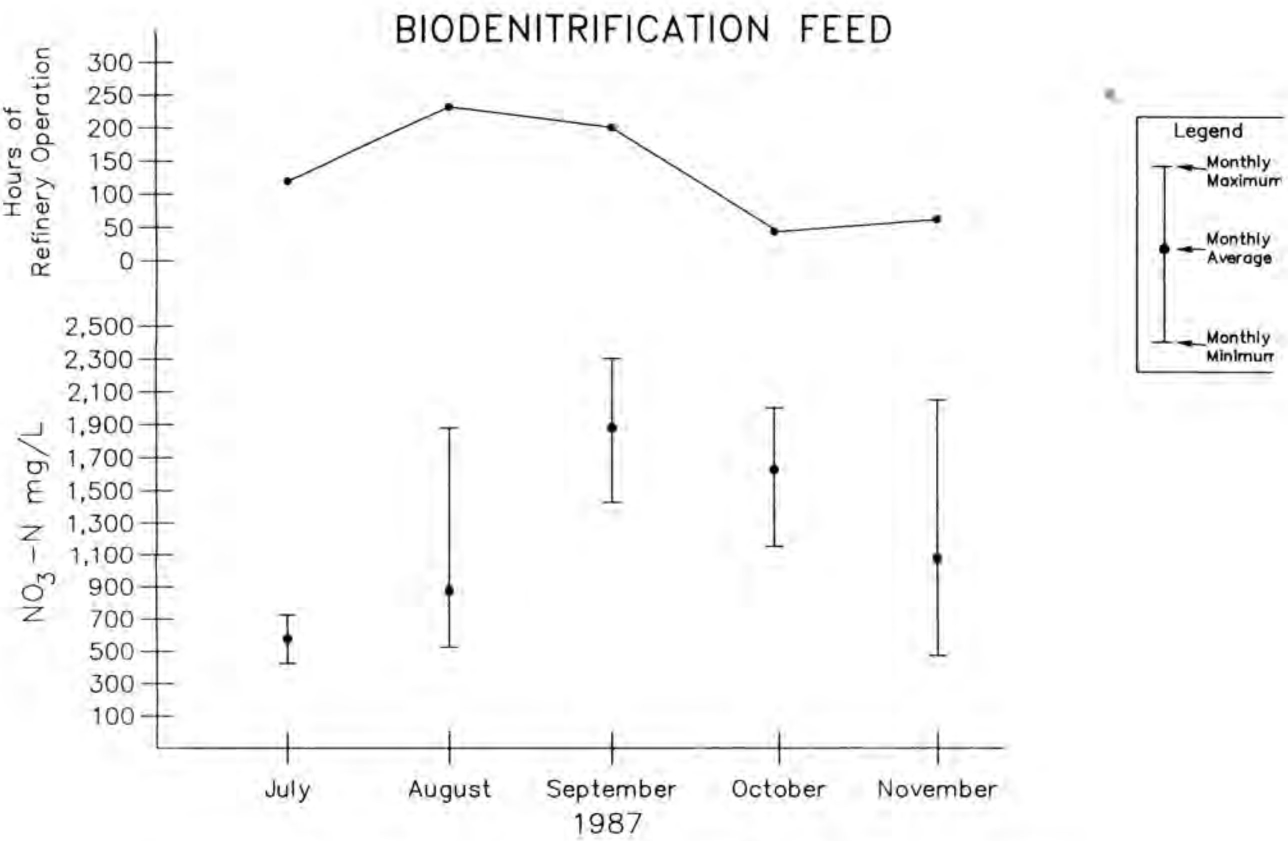

Fig. 3. Nitrate Nitrogen Feed Concentration and Hours of Refinery Operation.

The raffinate may be stored where it is produced or it may be stored at the General Sump, and time is required for it to pass through the BSL. For example, if the values for refinery hours of operation are lagged by one month when compared to BSL nitrate nitrogen concentration (i.e., refinery hours for July are compared to BSL concentration in August), an R^2 value of 0.85 results. This is evidence of a high linear correlation.

Figure 4 is a presentation of denitrification data for the July through November, 1987, period of operation. The BDN continued to meet or exceed the performance reported during the demonstration test which ended July 2, 1987. Denitrification peaked in September, coinciding with a peak in nitrogen feed rate. October had the lowest denitrification rates, caused by a reduction in flow to the BDN. This reduction was made in an effort to conserve the remaining water accumulated in the BSL. (It is necessary to leave a minimum 7,600 cubic meters of wastewater in the BSL during winter to protect the underlying bentonite clay liner of the lagoon from freezing.)

The limits established for the BDN effluent are 62 kg/day nitrate nitrogen as a 30-day average and 124 kg/day as a daily maximum. Prior to the startup of the BDN, the FMPC generated in excess of 500 kg/day of nitrogen for disposal. In July, 1987, the BDN came into compliance with the limits and continued in compliance through November (Fig. 5). A peak in nitrogen discharge was observed in September which was marked by the highest denitrification rates achieved thus far by the BDN.

BDN EFFLUENT

The biodenitrification facility outfall is regulated only for nitrate as nitrogen (see Table I). With this in mind, the BDN was initially operated by taking into consideration only the excess hydraulic capacity of the downstream sewage treatment plant (STP). During a very short period of BDN operation in Fall, 1986, the effluent from the BDN was sent directly to the sewage treatment plant which immediately began experiencing upset conditions. This upset was identified at the time as being due to the release of entrained nitrogen and carbon dioxide gases from the BDN effluent when it flowed into the STP.

Start-up of the BDN in April through May, 1987, was done with the effluent being recycled to the BSL. In June,

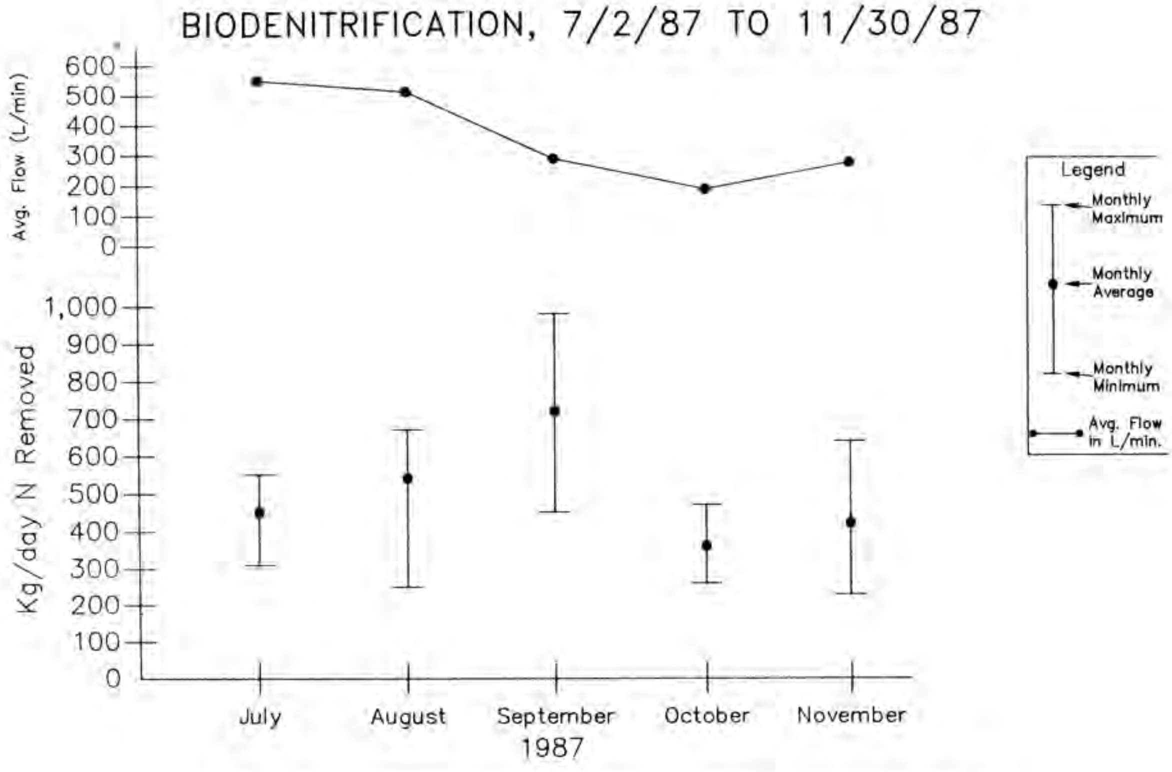

Fig. 4. Total Nitrogen Removed (Kg/day) and BDN Feed Flow (L/min.).

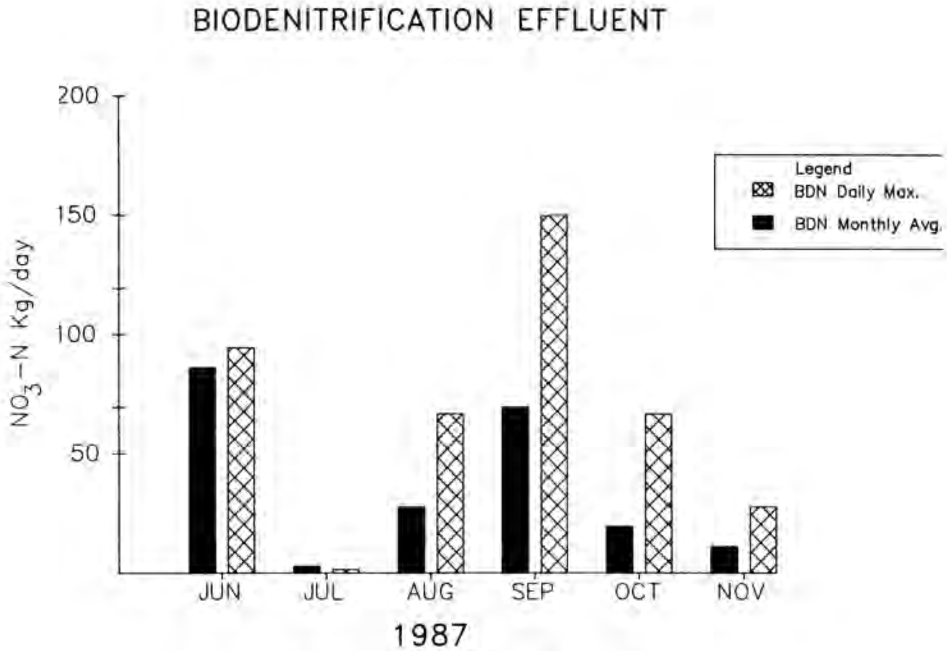

Fig. 5. Total Nitrogen Discharged.

TABLE I

Design Parameter Limits

FMPC Liquid Effluents

Source	BOD Daily Avg.	BOD Daily Max.	TSS Daily Avg.	TSS Daily Max.	Nitrate (N) Daily Avg.	Nitrate (N) Daily Max.
Manhole 175			20 (mg/L)	40 (mg/L)	1590* (kg/day)	3180* (kg/day)
Sewage Treatment Plant	5 (kg/day)	10 (kg/day)	5 (kg/day)	10 (kg/day)		
Biodenitrification Effluent					62** (kg/day)	124** (kg/day)

* Limits expired 6/30/84
** In effect since 7/1/84

BDN effluent was sent to the STP after preaeration to strip out entrained gases. Discharge concentrations of STP effluent BOD_5, TSS, and FC increased (see Table 1) beginning in July, 1987. The excessive BOD_5 concentrations were caused by the poorly controlled addition of methanol. Once the impact of the BDN on the STP was realized, several procedures were implemented to control the BOD_5 concentrations.

Calculations showed that aeration could strip some of the excess methanol from the BDN effluent and provide some BOD_5 removal through biological activity. This was accomplished using an air sparger installed in Tank 8 of the General Sump until a more efficient jet-eddy aerator was procured and installed. The other method for controlling the BOD_5 entering the sewage treatment plant was to minimize the amount of excess methanol being added to the BDN influent. Control of this parameter began in early July, 1987, with the installation of a more accurate methanol feed metering system. Additional control was also obtained in late August with the addition of two pressure-regulating valves on the BDN feed line.

The process control data taken for the period July through September, 1987, reported BOD_5 data only for the BDN effluent after it had been aerated in Tank 8. The BDN demonstration test concluded that some form of effluent treatment would be required in order to avoid overloading the sewage treatment plant (2). In September, additional BOD_5 data was obtained for effluent treatment design purposes.

Review of the data for the period of July through November, 1987, shows a direct relationship between methanol control and Tank 8 effluent BOD_5. This relationship is illustrated in Figure 6.

As can be seen from Figure 6, the poorly controlled addition of methanol throughout July resulted in very high concentrations of BOD_5 leaving Tank 8 and consequently overloading the sewage treatment plant. As further control of the methanol feed was accomplished throughout August and September, the effluent BOD_5 concentrations also dropped. The corrective actions taken thus far to correct the methanol feed fluctuations have greatly reduced the impact of the BDN effluent on the sewage treatment plant (see Fig. 7).

A complete characterization of the effluent from the BDN facility has yet to be accomplished. This information will be required for the design of an adequate effluent treatment system which is to be included in the upgrade of the BDN facility to a permanent four-column production facility.

A preliminary study indicated that the influent to the sewage treatment plant may exhibit toxic inhibition of the trickling filters currently being used at the plant. Because it is not clear whether this effect is being produced by the BDN facility or some other stream entering the STP, an in-depth treatability study is to be performed. In order to establish whether activated sludge treatment will be an effective form of BDN effluent treatment, a detailed pilot scale study will be performed using a bleed stream from the BDN system effluent line so that actual effluent stream concentration fluctuations will be accurately represented.

It is anticipated that this effluent treatment system will be a stand-alone activated sludge treatment facility and that a pre-engineered/package treatment system of proven ability can be used to treat BDN effluent. Because the bioreactors operate in an anoxic state, there will probably be a need for a preaeration step prior to treating the BDN effluent in a fully aerobic system. Preliminary screening tests show that the BDN effluent contains fecal coliform (FC) bacteria. The presence of FC will necessitate the disinfection of the final effluent prior to discharge to the Great Miami River.

SUMMARY

The BDN continued to meet or exceed the performance previously reported during the demonstration test (2). Denitrification peaked in September, 1987, coinciding with a peak in nitrogen feed rates. October had the lowest denitrification rates, caused by a reduction in flow to the BDN. Operation of the BDN resulted in compliance with the design limits for nitrate in July, 1987. Substantial compliance continued through November, 1987, with a peak in September, 1987, which coincided with a peak in nitrogen feed rates.

The FMPC refinery operation has the largest impact on the amount of nitrate requiring treatment by the BDN. Neutralized raffinate filtrate is approximately 4% of total process wastewater but represents 45% of the total nitrate load on the BDN. Early in the operation of the BDN, it became apparent that the BDN surge lagoon was inadequate for providing concentration equalization. The BDN feed nitrate concentration continued to fluctuate widely throughout this period of operation.

The BDN was initially operated taking into consideration only the excess hydraulic capacity of the downstream sewage treatment plant (STP). In June, BDN effluent was sent to the STP after preaeration to strip out entrained gases. BDN effluent caused a doubling of the hydraulic loading and a tripling of the organic loading on the STP. This resulted in increased discharges of BOD_5, TSS and Fecal Coliforms (FC) from the STP. Measures were taken in July and August, 1987, to control the methanol feed to the BDN. These measures, coupled with reduced flow, improved preaeration and operational changes, caused a sig-

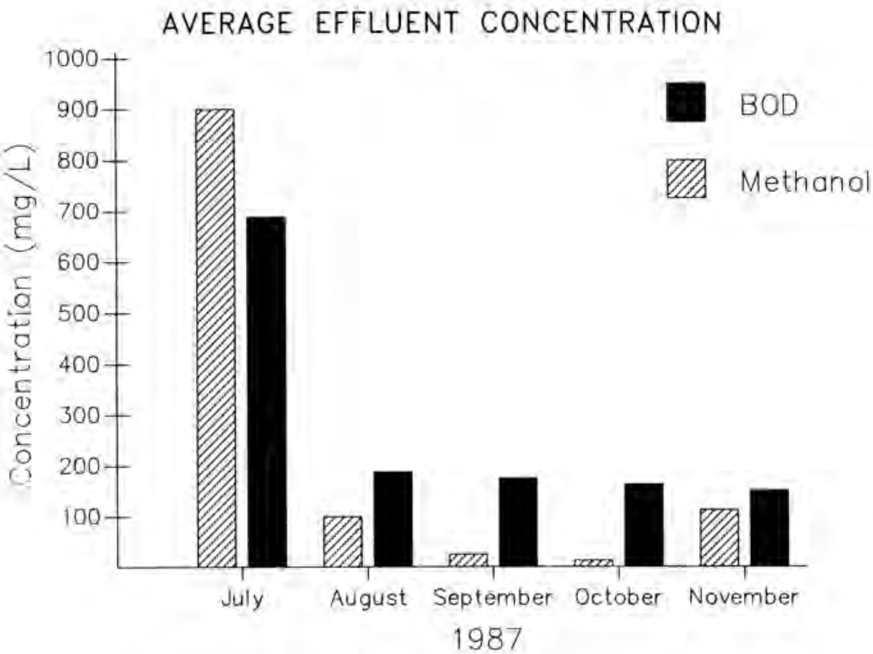

Fig. 6. Effluent Methanol and BOD Concentrations.

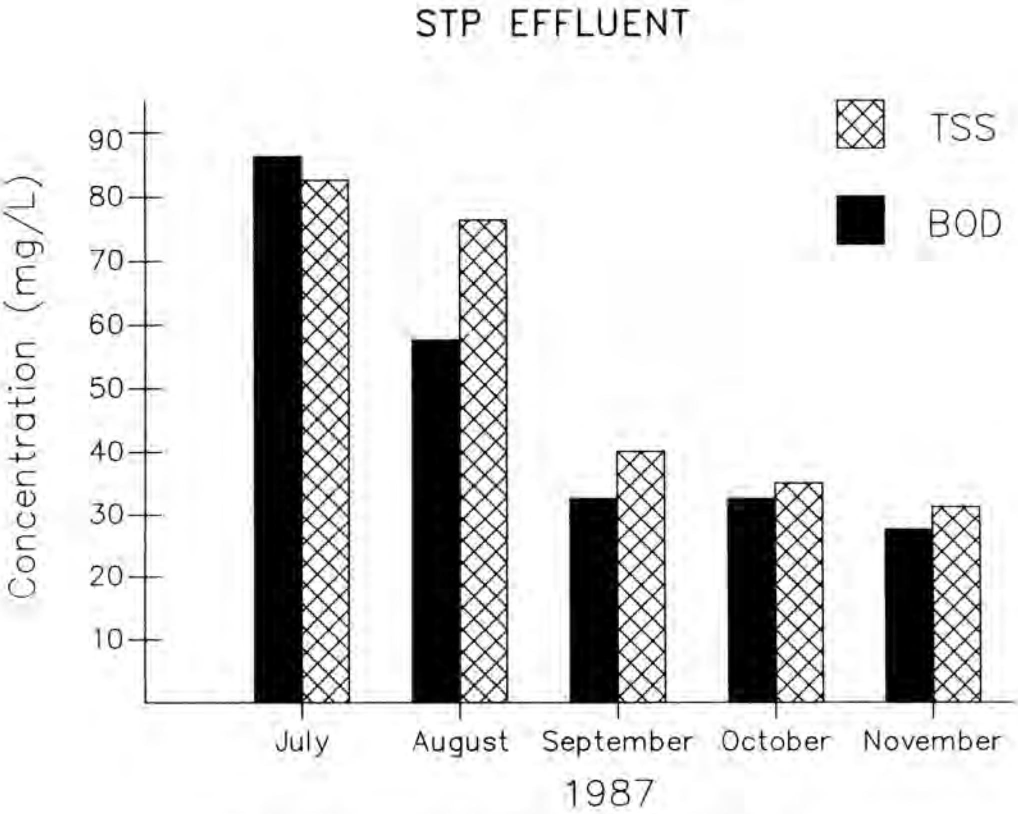

Fig. 7. 30-Day Averages, BOD and TSS Discharge.

nificant improvement in the effluent quality of the STP with BOD5 and TSS.

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Preliminary screening tests show that the BDN effluent contains fecal coliforms which will necessitate the disinfection of the final effluent prior to discharge to the Great Miami River. The BDN effluent data, including Fecal Coliform data, will be used to design a new BDN effluent treatment system which will be constructed as part of the BDN facility upgrade to a permanent four-column production facility.

REFERENCE

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2. A. K. Benear, et. al., "Biodenitrification Demonstration Test Report, FMPC-2095, Westinghouse Materials Company of Ohio