START-UP AND OPERATION OF THE BIODENITRIFICATION DEMONSTRATION FACILITY AT THE FMPC

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ABSTRACT

The chemical processes used at the U. S. Department of Energy's Feed Materials Production Center (FMPC) result in waste streams containing high concentrations of nitrates. A fluidized bed biodenitrification system has been designed and constructed to demonstrate that the reduction of nitrates using a production scale reactor is feasible. The technology is based on pilot scale studies performed at the Oak Ridge National Laboratory.

Design and construction of a two-column biodenitrification system has been completed at the FMPC. Through the efforts of a dedicated start-up team, and utilizing an operational readiness review methodology, the demonstration facility has been placed in operation. The operation is following a formal performance monitoring and assessment plan. Data collection and performance assessment in the early phases of the demonstration test has been initiated. Preliminary performance results at low flow rates and low nitrate concentrations are presented. Demonstration testing is expected to be completed in June 1987.

INTRODUCTION

The Feed Materials Production Center (FMPC) uses a wide variety of chemical and metallurgical processes to convert recycled materials (furnished internally and from other DOE sites) into uranium metal products. These products are used in the U. S. Department of Energy (DOE) defense programs and consist of uranium oxides or machined ingots and billets for the fabrication of fuel cores and target fuel elements.

The chemical processes utilized consist of dissolving materials in nitric acid and results in raffinate solutions containing high concentrations of nitrates. The control of nitrate discharge is regulated by the National Pollutant Discharge Elimination System (NPDES). Several nitrate reduction processes are being pursued at the FMPC, one of which is the biodenitrification (BDN) fluidized bed system. This report describes the progress made to date in demonstrating the design, construction, start-up and performance testing for a production scale BDN unit at the FMPC.

DISCUSSION

FMPC Background

The FMPC, owned by the DOE and operated by the Westinghouse Materials Company of Ohio (WMCO) is located in Fernald, Ohio. The mission of the FMPC is the production of uranium metal used primarily for fuel in the production reactors at Hanford, Washington and Savannah River, South Carolina.

Chemical operations at the FMPC include dissolving various uranium compounds in nitric acid to produce a uranyl nitrate (UNH) feed solution for solvent extraction purification. Purified UNH solution is concentrated by evaporation and then thermally denitrated to uranium trioxide (UO_3), or orange oxide. Nitrogen oxides released during the dissolution and denitration steps are captured, converted to nitric acid and reused in the process. Orange oxide is converted to uranium tetrafluoride (UF_4), commonly called green salt, for reduction to metal at the FMPC. Scrap materials generated in FMPC operations and those received from off-site are upgraded to chemical processing requirements by furnacing operations. Small-scale facilities exist for performing similar chemical process operations for enriched materials assaying up to 20% ^{235}U. Facilities are also in operation for converting UF_6 to UF_4 green salt for subsequent reduction to derby metal.

Metal processing steps begin with the conversion of green salt to elemental uranium (derby metal) by reducing UF_4 with magnesium metal. Metallic scrap and briquettes, recycled from subsequent fabrication operations, are combined with derby metal and melted in a graphite crucible. At the proper temperature, the metal is bottom-poured to a preheated graphite mold to form ingots, varying in weight, size and shape according to their ultimate use. Cast ingots may be rolled to rod at the FMPC or machined for extrusion into tubes at the RMI Company. Since the late 1960s, all ingots have been machined for extrusion. Most tubes are returned to the FMPC for heat treating and final machining operations to produce target element cores for the Savannah River Plant. Some extrusions are processed at RMI to produce billets for co-extrusion at Hanford.

A flow diagram of the FMPC process is given in Fig. 1.

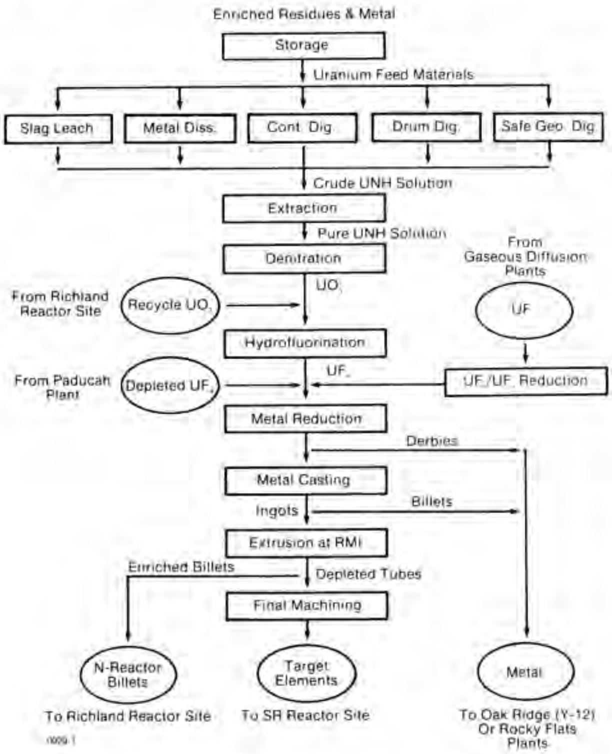

Fig. 1. Schematic Diagram of the FMPC Process.

Waste Streams

Several waste streams result in the course of production activities at the FMPC. Waste streams are collected in the plant general sump area prior to being diverted to the biodenitrification system. The major sources of nitrate-bearing waste are shown in Figures 2 and 3.

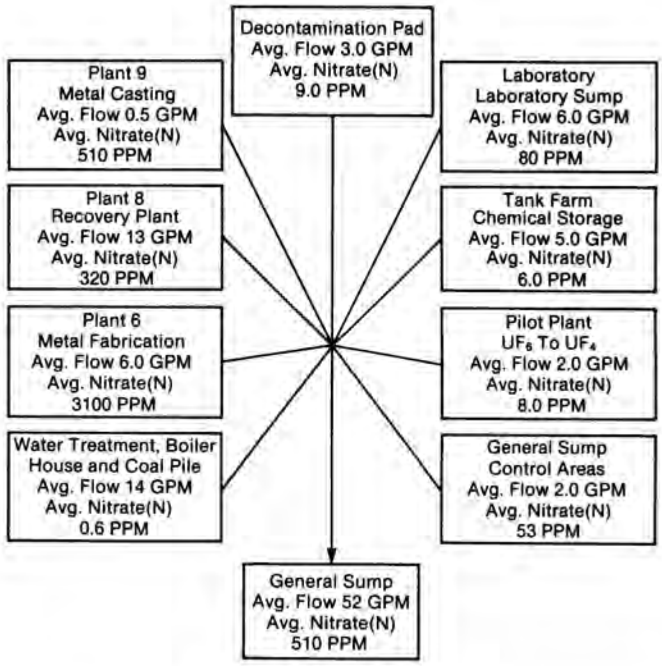

Fig. 2. Average Sump Flows and Nitrate (N) Concentrations (Refinery not in Operation).

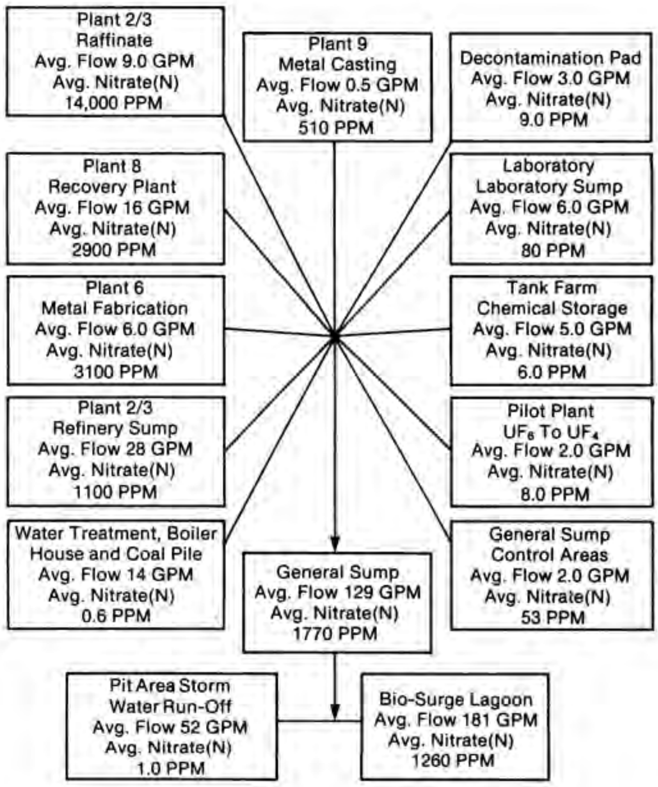

Fig. 3. Bio-surge Lagoon Influent Flows and Nitrate (N) Concentrations During Refinery Campaign.

The primary source of high concentrations of nitrates comes from the digestion and extraction processes in the refinery operation. The refinery is operated intermittently in a sequential campaign mode throughout the year. Raffinate solutions containing nitrate (nitrogen) levels as high as 23,000 g/m^3 are produced by the refinery.

The BDN system is expected to routinely see an average flow of 3.16×10^{-3} m^3/sec (50 gpm) at an average nitrate/nitrogen concentration of 510 g/m^3 increasing to 1.14×10^{-2} m^3/sec (180 gpm) and 1260 g/m^3 of nitrate (nitrogen) during periods of refinery campaign operations.

Experimental Studies

Design of the biodenitrification facility at the FMPC was based on pilot work performed at the Oak Ridge National Laboratory (ORNL). Since design of the FMPC facility involved the extrapolation of the ORNL results to both significantly larger scale equipment and to actual rather than synthetic wastewaters, design verification studies were performed by ORNL (May - August 1985) to reduce uncertainties associated with the process. Results of the design verification studies indicated that high probability of serious problems associated with the process could preclude operation of the full scale system as designed. As a result, a development program was initiated to provide answers to the remaining questions regarding the FMPC biodenitrification system.

In the fluidized bed bioreactor process developed at ORNL, bacteria were allowed to grow and attach to 30-60 mesh anthracite coal particles to form "bioparticles." The wastewater was pumped through a bed of bioparticles at a velocity sufficient to fluidize the bed. As the wastewater flows past the bioparticles, the nitrate degrades to N_2 and CO_2 gas which is vented to the atmosphere. The ORNL studies demonstrated that the FMPC design denitrification rate of 32 kg $NO_3(N)/m^3d$ could be achieved. Process requirements for multipoint pH adjustment and softening of the feed stream were also identified as additional criteria.

Demonstration Program

The purpose of the demonstration program at the FMPC is to integrate the experimental results into a large scale unit prior to completing the design of a full production unit facility. The objectives of the demonstration test are as follows:

1. Determine the achievable rate of biodenitrification

2. Evaluate methyl alcohol consumption (bacterial substrate) rate

3. Confirm sulfuric acid requirements (pH adjustment)

4. Evaluate accommodation of the biomass by the FMPC sewage treatment facility

5. Evaluate the flexibility of the system to receive waste streams which vary in both volume and nitrate concentration

6. Determine new modifications and/or additions needed in the system to function as a permanent production facility.

Figure 4 illustrates the biodenitrification process. High nitrate-containing waste streams are collected from several process areas where each stream has been neutralized and filtered prior to being sent to the general sump. These streams are combined in the plant general sump. The effluent from the sump area is passed through two existing settling basins (Pit 5 and the clearwell). This flow would normally go directly to the discharge outfall into the Great Miami River. With the implementation of the BDN system, this stream will now be processed through a surge lagoon, a buffering step, and then to the bioreactors. The denitrated effluent from the bioreactors is then processed by the existing FMPC sewage treatment plant before being finally discharged to the outfall.

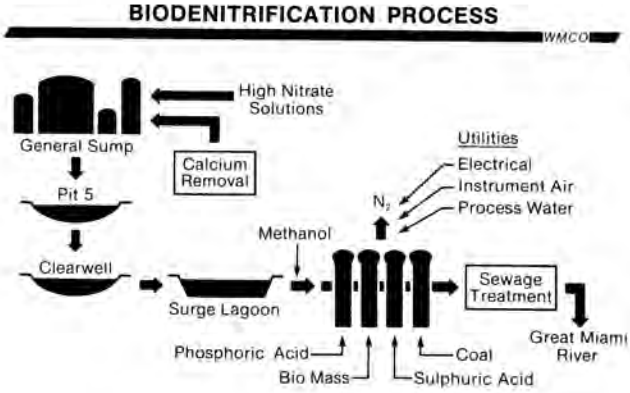

Fig. 4. Biodenitrification Process.

Figure 5 shows a detailed schematic of the two-tower BDN system with instrumentation and sample points being used during the demonstration test. The demonstration sequence is given below:

Complete construction - two tower system
Preoperational check-out
Incubate and run
Test data collection
Data analysis
Prepare test report
Validate redesign parameters.

Currently, the construction of the two-tower demonstration facility has been completed, bacteria incubation has been performed, and test data collection at low nitrate concentrations and flows has been initiated.

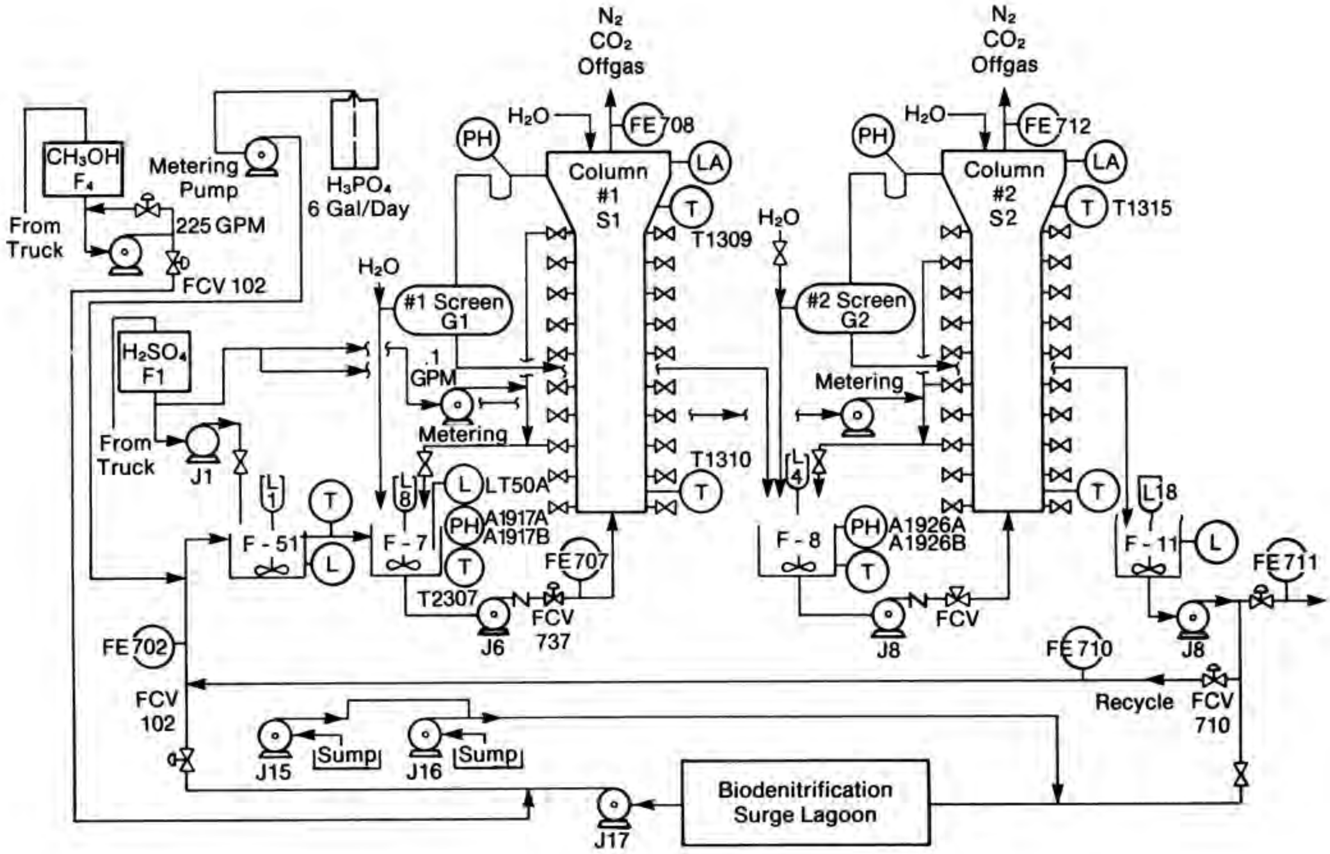

Fig. 5. Biodenitrification Facility.

Start-Up Coordination and Readiness Review

To facilitate start-up of the BDN demonstration unit, a dedicated team was assembled to provide the logistical coordination of the activities required to design, construct, operate and test the unit. The make-up of the team consisted of representatives from all involved project participants. Operations personnel were fully involved in formulating plans. The quality organization and the project engineer from the construction contractor were also an integral part of the team. A team leader was established and had the responsibility and authority to obtain the resources and funding to properly implement the start-up activities. Weekly coordination meetings were held by the team to identify functions, assign action items, and status and control activities. Routine field sessions were held to keep the program moving and address problems in a timely manner. The structure of the start-up coordination team is shown in Fig. 6.

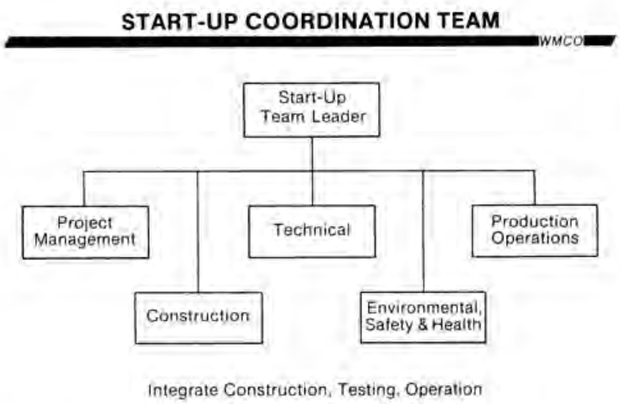

Fig. 6. Integrate Construction, Testing, Operation.

A readiness review methodology was used by the start-up team to facilitate a successful startup. Operational Readiness Review (ORR) is a structured, logistical technique to define the total list of activities required to place a facility into operation through the development of a management oversight tree. Three basic categories, procedures, personnel and hardware (see Fig. 7), form the hierarchy to expand the tree to the lowest level of detail necessary. Once the oversight tree is developed, assignment and responsibility tracking matrices can be prepared and used to follow progress and activity completions until final readiness is achieved. A schematic of the biodenitrification ORR oversight tree is presented in Fig. 8. This tool proved to be very useful in the start-up effort.

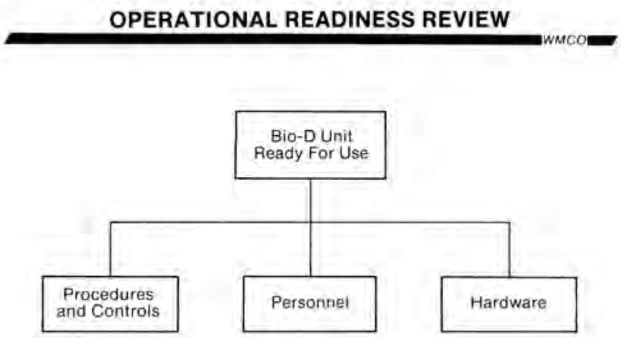

Fig. 7. Operational Readiness Review.

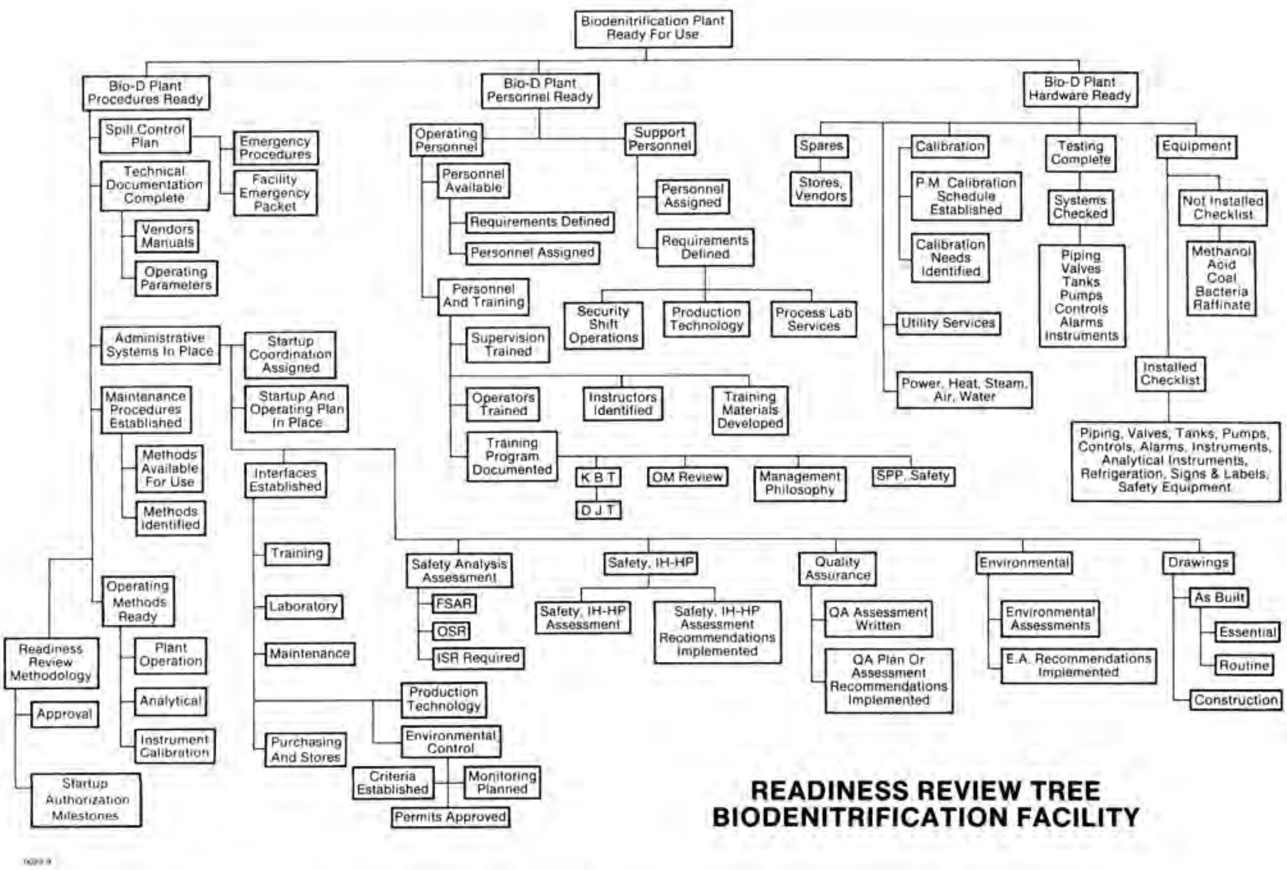

Fig. 8. Readiness Review Tree Biodenitrification Facility.

Equipment and Process Description

The FMPC biodenitrification system consists of four columns, each four feet in diameter, expanding to seven feet *in* diameter in the top section. The total height of each is 52 feet. At the bottom are nine entry ports and near the top is a single overflow discharge. A trap is installed in the overflow line to provide a gas-phase seal so that the generated off-gas can be measured prior to ventilating.

The wastewater flows through each column in series. The upward flow within each column is 150-200 gpm which is sufficient to provide fluidization of the very small coal particles (0.25 - 0.50 mm) to which the bacteria are attached. The residence time of the wastewater within each column is 20-30 minutes.

The initial demonstration program utilizes all auxiliary facilities and two of the four columns. The auxiliary equipment includes: column feed tanks and pumps, premix tank, discharge tank, sulfuric acid supply system, methanol supply tank and metering system and a wastewater surge lagoon (8.5 million gallons capacity).

Demonstration Test Description

The demonstration test was conceived to show the viability of the process, for as much of the system as the construction budget would allow, prior to committing additional funds for the completion of the total job. The test performance, therefore, includes operating the two columns in their normal fashion as designed, using the process wastewater from the entire plant, and demonstrating design throughput while achieving the target denitrification rate. The facility operates seven days a week with the intention of raising the rate of denitrification to a level as high (or higher) as was achieved in the development of the process. The target rate of denitrification is 32 kg $NO_3(N)/m^3d$. For the volume of our columns, this rate becomes 500 kg $NO_3(N)$/day for each column. The nitrate concentration is monitored at several locations throughout the system to determine progress in achieving the target denitrification rate.

The principal source of nitrates in the process wastewater stream is our refinery which has recently begun operation after an extended shutdown. The wastewater stream is now increasing in nitrate concentration so that the FMPC demonstration test will be conducted under conditions of increasing nitrate concentrations as well as a steady-state high level.

Process Control

The flow within the system is set initially as a combination of the internal recycle stream and the incoming stream from the surge lagoon. The individual flows to each column are controlled by the level indicator of each column feed tank so that "whatever goes in, goes out." Discharge from the system to the sewage treatment plan is at a controlled rate with the excess flow, if any, being returned to the surge lagoon ("extral cycle"). Therefore, each system is independently controlled.

Alcohol is added to the line feeding the columns from the surge lagoon in proportion to the nitrate concentrations. Sulfuric acid is added at several locations in the system to provide pH adjustment as required.

Hourly records are maintained of process conditions throughout the system. A typical data sheet is shown in Fig. 9.

SHIFT DATA SHEET

Date: ________
Shift: ________
Operator: ________
Supervisor: ________

Measurement	Target Value	Hourly Readings 1	2	3	4	5	6	7
Trailer Instrumentation								
Premix Tank Inflow FIC702								
Premix Tank pH AIC913								
No. 1 Feed Tank Level LIC504								
No. 1 Feed Tank pH AIC917								
No. 1 Column Inflow FIC707								
No. 1 Column Top pH AIC973								
Column No. 1 Offgas FIR712								
Column No. 2 Offgas FIR708								
No. 2 Feed Tank Level LIC507								
No. 2 Feed Tank pH AIC925A								
No. 2 Column Inflow FIC716								
No. 2 Column Top pH								
Effluent Flow Rate FIR7118								
Effluent Tank Level LIC512								
Effluent Flow Rate FIC711								
Internal Recycle Flow FIC710								
Premix Tank Temp.								
No. 1 Feed Tank Temp.								
Ambient Temp.								
Methanol Flow								
Acid Metering Pump Setting								
Premix Tank								
No. 1 Feed Tank								
No. 2 Feed Tank								
No. 1 Column Level 1								
No. 1 Column Level 2								
No. 1 Column Level 3								
No. 1 Column Level 4 (Top)								
No. 2 Column Level 1								
No. 2 Column Level 2								
No. 2 Column Level 3								
No. 2 Column Level 4 (Top)								
Phosphoric Acid								

Special conditions or instructions

Fig. 9. Shift Data Sheet.

Test Data

Samples are routinely taken every eight hours and analyzed to monitor process conditions and denitrification rates. This data is not required for process control and is not available to us until more than 24 hours after the fact. Analytical data determined includes:

1) divalent cations (Ca^{+2}, Mg^{+2})

2) monovalent cations (Na^+, K^+, NH_4^+)

3) anions (NO_3^-, NO_2^-, CO_3^{-2}, SO_4^{-2}, PO_4^{-3})

4) gas analysis (%N_2, %CO_2, CH_4)

5) alcohol.

These results are being collected for correlation with data obtained during development of this process at ORNL to aid in determining the comparative performance of this production scale system to the development units.

The experience of the FMPC thus far has shown a much more uniform feed is delivered to the production columns than was the case with the test columns. A more sophisticated control system is currently being employed than previously used in development testing and operation is principally automatic.

The following two data plots show initial start-up conditions. Figure 10 gives the mass flow of NO_3(N) into the first column, out of the first column, and out of the second column. It is apparent that nearly all of the nitrates were decomposed in the first column. The off-gas record was superimposed on the same plot (cubic feet per minute x 100) to show the correlation of nitrate removal and off-gas generated.

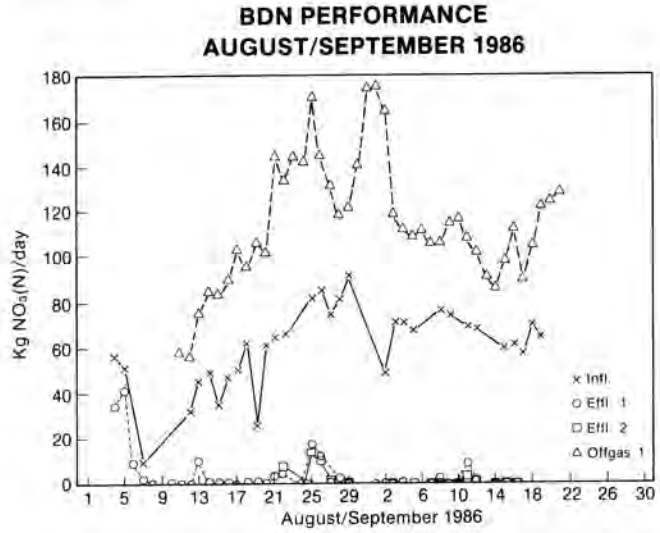

Fig. 10. BDN Performance.

Figure 11 shows the three principal anions in the solution discharged from the #1 column. Both of these graphs cover the initial six months of startup of the BDN system. Unfortunately, the BDN system was then shut down to await the increase in wastewater nitrate concentration from our refinery operation and the satisfactory completion of the surge lagoon. During January 1987, the BDN was re-started.

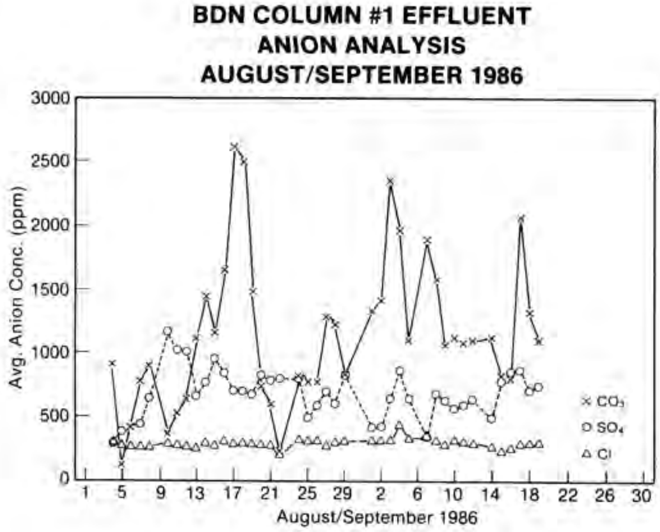

Fig. 11. BDN Column #1 Effluent Anion Analysis.

ALTERNATIVE ROUTES FOR BDN

Biological decomposition of nitrates has been conducted over a range of concentrations from very low values (drinking water treatment) to extremely high values (wastewater treatment at the Y-12 DOE plant). The FMPC wastewater stream more closely resembles that of the Y-12 plant but with some differences as illustrated in Fig. 12.

BDN

"Stirred Tank"		"Fluidized Column"
0.5 - 1.0 GPM	Flow	150-200 GPM
65,000/≤50 PPM	Concentration In/Out	1000-2000/<100 PPM
15 Days	Residence Time	Two Hours
7 - 8	pH	7 - 8
40 - 50°C.	Temperature	30 - 40°C.
Ca + Al Sludge Precipitated		No Solids Accommodated

Fig. 12. Biodenitrification Options.

The denitrification load capacity (200 kg NO_3(N)/day) of the FMPC system is approximately ten times the original stirred tank unit at Y-12. Additional larger units are now in operation. The principal differences, however, are in the flow and nitrate concentration of the entering stream of each system. The stirred tank system handles particularly well the extremely high nitrate concentrations in a small acidic stream whereas the fluidized column can better accommodate the very large flow which is more dilute. The FMPC refinery raffinate stream even more closely resembles the Y-12 waste stream but the other waste stream also contain significant nitrate levels which must be processed so that the need remains for a high volume capacity system.

FUTURE STUDIES

This demonstration test will extend through June 1987 to complete the demonstration test program described earlier. As additional funding is made available, the permanent production facility will be constructed and put into service. Undoubtedly, additional facets of this technology will continue to be explored as fluidized column biodenitrification becomes an additional option in waste water treatment.