ADVANCED BIOLOGICAL TREATMENT OF AQUEOUS EFFLUENT
FROM THE NUCLEAR FUEL CYCLE

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INTRODUCTION

Many of the processing steps in the nuclear fuel cycle generate aqueous effluent streams bearing contaminants that can, because of their chemical or radiological properties, pose an environmental hazard. Concentration of such contaminants must be reduced to acceptable levels before the streams can be discharged to the environment. Two classes of contaminants, nitrates and heavy metals, are addressed in this study. Specific techniques aimed at the removal of nitrates and radioactive heavy metals by biological processes are being developed, tested, and demonstrated. Although cost comparisons between biological processes and current treatment methods will be presented, these comparisons may be misleading because the biological processes yield environmentally better end results which are difficult to price.

Sources of nitrates and heavy metals

It has been estimated that as much as 2.5 million tons of dissolved nitrogen-bearing substances reach the surface waters of the U.S. each year.[1] The nitrogen waste discharged directly from industrial installations is estimated to be about 20% of the total.[2] Much of this nitrogen pollution is in the form of dissolved nitrates at high concentrations. These high concentrations can contribute to eutrophication[3] and can also constitute a health hazard.[4] Consequently, rigorous standards are being established for nitrates released in industrial effluents (e.g., the Department of Energy's

Y-12 Plant at Oak Ridge, Tennessee is restricted to 45 g/m^3 as N), and there are indications that these restrictions will become even more stringent, perhaps as low as 10-15 g/m^3 as N in most states. Although the majority of industrial nitrate pollution is attributed to fertilizer and paper manufacturers, liquid effluents from the nuclear fuel cycel contribute significantly to the total problem. Process steps in the uranium fuel cycle (Fig. 1) that generate nitrate wastes and include milling, refining and conversion, enrichment, fuel fabrication, and fuel reprocessing operations. Disposition of the nitrate (recovery, conversion, or discharge) will be governed by the economics of the process technologies which may be applied. In situations where nitrate recovery is not feasible, conversion of all nitrogen oxides, including NO_x, to molecular nitrogen (chemically or biochemically) appears to be the only acceptable long-range solution.

Many operations in Department of Energy and commercial nuclear processing facilities also generate aqueous waste streams which contain trace quantities of dissolved heavy metals, including radionuclides (Fig. 1). There are a number of physical and/or chemical methods for isolating heavy metals from aqueous streams including chemical precipitation, chemical oxidation or reduction, ion exchange, filtration or ultrafiltration, electrochemical treatment, and evaporative recovery. However, when the initial heavy-metal concentration is in the range of 10-100 g/m^3 and a reduction to less than 1 g/m^3 must be achieved, such methods may be ineffective or uneconomic. In such situations, the adsorption of dissolved metal species by microorganisms offers a safe and economical means of achieving a reduction in dissolved metal concentration to less than 1 g/m^3.
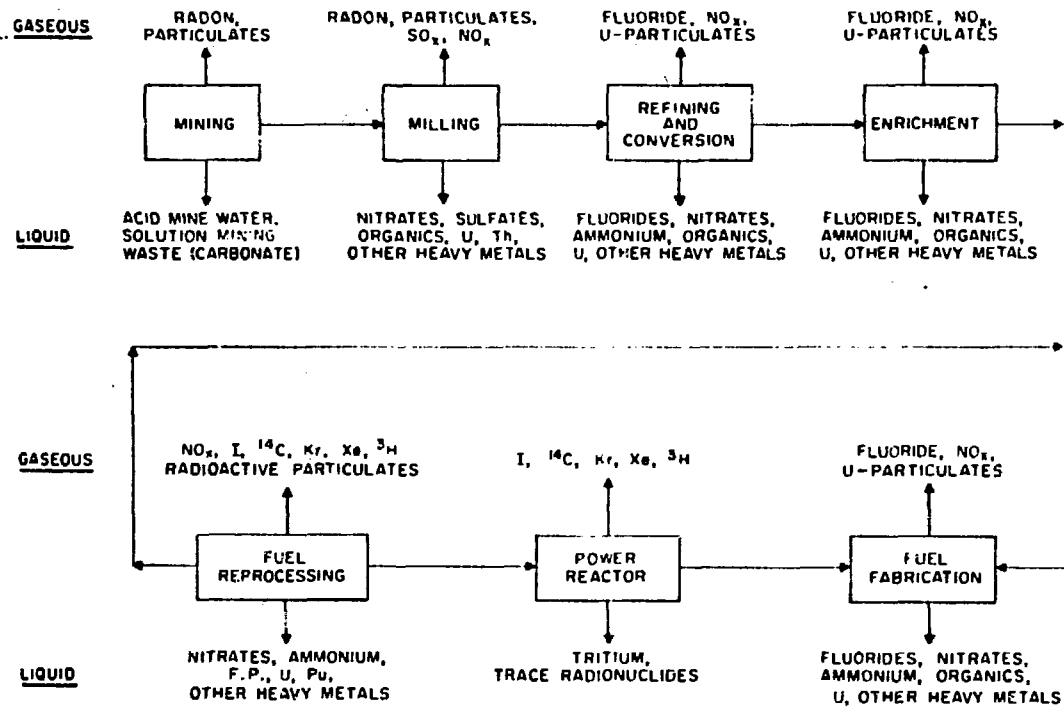
ORNL DWG 77-1852

GASEOUS — RADON, PARTICULATES | RADON, PARTICULATES, SO_x, NO_x | FLUORIDE, NO_x, U-PARTICULATES | FLUORIDE, NO_x, U-PARTICULATES

MINING → MILLING → REFINING AND CONVERSION → ENRICHMENT

LIQUID — ACID MINE WATER, SOLUTION MINING WASTE (CARBONATE) | NITRATES, SULFATES, ORGANICS, U, Th, OTHER HEAVY METALS | FLUORIDES, NITRATES, AMMONIUM, ORGANICS, U, OTHER HEAVY METALS | FLUORIDES, NITRATES, AMMONIUM, ORGANICS, U, OTHER HEAVY METALS

GASEOUS — NO_x, I, ^{14}C, Kr, Xe, ^3H RADIOACTIVE PARTICULATES | I, ^{14}C, Kr, Xe, ^3H | FLUORIDE, NO_x, U-PARTICULATES

FUEL REPROCESSING → POWER REACTOR → FUEL FABRICATION

LIQUID — NITRATES, AMMONIUM, F.P., U, Pu, OTHER HEAVY METALS | TRITIUM, TRACE RADIONUCLIDES | FLUORIDES, NITRATES, AMMONIUM, ORGANICS, U, OTHER HEAVY METALS

Fig. 1.   Some effluent waste streams in the uranium fuel cycle.

Regulations

Industrial liquid waste discharges are controlled by the Federal Environmental Protection Agency (EPA), state water quality boards, and, occasionally, local regulations. The EPA issues effluent discharge permits under the National Pollutant Discharge Elimination System (NPDES). The NPDES permit authorizes a plant to discharge into a specified waterway from a set number of outfalls. Usually, the permit also sets limits on specific effluent parameters, e.g., flow rate, maximum BOD_5, minimum dissolved oxygen, temperature ranges, etc. Sampling and analysis frequency are often specified. Wastewater components such as BOD_5 may be limited in concentration, in total mass discharged per day, or both. The NPDES permit is usually issued for a period of 5 years.

Most states have water quality control boards which also issue discharge permits. Some states issue permits jointly with the EPA, while other states issue separate state licenses, sometimes with stricter limits than the NPDES. Still others issue no permits at all, but expect plants to adhere to the NPDES limits. Cities and towns sometimes have statutes concerning effluents from local plants, but these are usually concerned exclusively with effluents discharged to municipal sanitary sewers. Some cities allow plants to dump high-BOD wastes to sanitary sewers, for example, but charge the plant a monthly fee based on the total BOD dumped during the month.

At present, there are no nationwide standards for limiting nitrate in wastewater. There are indirect limits on excessive nitrate discharges, such as one regulation which states "Other pollutants shall not be added to the water in quantities that may be detrimental to public health or impair the usefulness of the water as a source of domestic water supply."[5] The state of New York considers 10 mg/L of nitrate to be the upper limit for potable water.[6] There are, however, few limits on the amount or concentration of

nitrates actually leaving plant outfalls. It is expected that some limits will be uniformly imposed by 1983, but the anticipated limits are now known at this time.

Discharges of heavy metals are more tightly controlled than nitrates at this time. Several nuclear facilities have metals limits in their NPDES or state permits, but exact numbers vary from state to state, and within a state, limits will vary between plants and even between different outfalls of the same plant depending upon location, receiving water, other pollutants discharged, etc. Sometimes a state will require reporting of certain metal levels, but has no actual limit set in the permit. Some common elements mentioned in permits include iron, chromium, nickel, copper, zinc, mercury, cadmium, aluminum, and radionuclides such as uranium, plutonium, and radium. It is likely that limits on heavy metals, in general, will become more standardized and more strict by 1983.

At present, there are very few treatment processes for nitrate wastes. Some of the current practices such as holding ponds and other dumping techniques can regulate the rate of discharge, but are not capable of reducing the amount of nitrate released. Other treatment practices include ion exchange, evaporation to NO_x, chemical decomposition using sugar or formaldehyde, and biological denitrification.

Atmospheric discharges of NO_x gases are severely restricted and, since there are no insoluble nitrate salts, it is thus impossible to precipitate a solid nitrate waste that can be buried. The only acceptable treatment method available is destruction of the nitrate ion, and the method commonly used is biological denitrification, which reduces the nitrate ions to nitrogen gas. Treatment of aqueous effluent to control heavy-metal releases generally

involves a concentration step followed by recovery of the metal or burial in a suitable form. Potential concentration methods include flocculation-clarification, ion exchange, and biological sorption, in addition to energy intensive evaporation.

NITRATE REMOVAL

Nitrate wastes are generated at many points in the nuclear fuel cycle (NFC). Nitric acid is very commonly used for radionuclide leaching, UO_2 or U_3O_8 dissolution, scrap recovery and cleaning, ion exchange bed regeneration, and other purposes. The stages in the fuel cycle which generate nitrate wastes include uranium milling, refining and conversion to UF_6, enrichment, fuel fabrication, and fuel reprocessing (Fig. 1). Currently, nitrates are elimi-nated by several methods, including some (calcining to nitrogen oxides, dumping wholly untreated, and storing in waste lagoons) which are likely to be severely restricted or banned in the near future.

Current discharge levels and disposal regulations for nitrate

A survey of 13 commercial and 14 DOE nuclear processing plants was conducted to obtain information on nitrate and heavy-metal disposal problems. State water quality boards and EPA regional offices were also contacted concerning legal limitations on nitrate and heavy-metal discharges from the 27 plants. Responses containing information on discharge permits, discharge monitoring reports, and a small amount of internal flowsheet data were received from 10 plants and 7 state offices. The following information is preliminary in nature since much of it is incomplete and some of the data are confidential. Therefore, no plant will be specified by name or location.

At present, much of the nitrate produced in the NFC plants surveyed is not discharged to the environment at all. Instead, it is stored indefinitely in liquid storage lagoons because it is either too concentrated or contains too many radionuclides to be released. Fuel fabrication and conversion plants generate large amounts of nitrate but discharge very small amounts; the remainder is sent to lagoons. The Oak Ridge DOE plants have discharged nitrate wastes by diluting them with large volumes of water to lower the concentrations. At least three plants have special permits to discharge 375 to 750 m^3/day (100,000 to 200,000 gal/day) of waste containing nitrate at levels of 2000 to 3000 g/m^3. Increased restrictions by EPA and state agencies will probably eliminate dilution or dumping options in a few years.

Responses from state and EPA offices indicate that, at the present time, there is no nationwide agreement on liquid discharge standards for nitrates. Most NPDES permits received did not mention nitrates or any other nitrogenous compounds. Nitrate or nitrogen limits were defined in two cases; the limit was on concentration in one, and on total mass discharged in the other.

Table 1 shows examples of nitrate limits in four states, as taken from the survey responses. The Ohio limits apply to any receiving waters; the limits in the other three states are taken from NPDES permits for specific NFC plants. Four other states that have NFC plants with no nitrate limits at this time are also listed. Some states have issued special permits for dumping wastes containing up to 3000 g of NO_3^--N per m^3, but these are considered to be temporary permits pending the installation of suitable waste treatment equipment. It is obvious that no general consensus on permissible nitrate levels has been reached. There are indications, however, that increasing concern over eutrophication effects and nitrate seepage into drinking water will soon encourage EPA, and probably most of the states, to set nitrate limits

T1

Table 1. Examples of some state limits on nitrate discharges

State	Substance limited	Limit	Remarks
North Carolina	Total nitrogen	35 kg/day (avg.) 50 kg/day (max.)	Applies to specific plant effluent
Ohio	Nitrate - N Nitrite - N	10 g/m^3 1 g/m^3	Applies to receiving waters outside the outfall "mixing zone," not to plant effluent
Oklahoma	Nitrate - N	19 kg/day (avg.) 77 kg/day (max.)	Applies to specific plant effluent
Washington	Nitrate - N	---	Plant required to report results, but limit not set
California Kentucky South Carolina Virginia			Plants in all these states have no nitrate limits specified in permits

on all liquid wastes. These limits will probably be under 30 g/m^3, and possibly as low as 10 to 15 g/m^3. Limits on total mass dumped will also probably be imposed to prevent simple dilution of the waste.

Current treatment processes for nitrate disposal

Methods of nitrate disposal currently in use at NFC plants include storage lagoons, dilution, and dumping, which have already been mentioned. Other methods include calcination and catalytic decomposition of NO_x to N_2, recycle, ion exchange, production of fertilizer, and some biological denitrification.

According to ORNL studies,[6,7] many NFC plants store nitrate wastes in lagoons for indefinite periods of time, as described previously. The obvious disadvantages of this solution are that the waste is never eliminated and that more and more land area must be devoted to lagoons. For example, it is estimated that a 1500-metric ton/year uranium fuel fabrication plant would require one 5700-m^3 (1.5 x 10^6-gal) lagoon to be dug every 6 months to contain its liquid wastes.[6] Also, lagoons would also present a hazard, under some conditions, if flooding occurred.

In the past, the Oak Ridge DOE plants have released their concentrated nitrate in small amounts at a time by diluting it with fresh water to 20 to 30 g/m^3. Although this may be a good short-term solution, regulatory agencies are frequently setting limits on the quantity of nitrate discharged as well as concentration, eliminating this practice of dilution. Other plants have special permits to dump 375 to 750 m^3/day (100,000 to 300,000 gal/day) of effluent containing 2000 to 3000 g of nitrate per m^3 into receiving waters. This cannot be done in areas with a heavy concentration of industry, and it is likely that such special permits will be totally revoked in a few years.

Recovery processes can often be successfully applied to waste streams that are reasonably free of impurities. For example, distillation systems are frequently used on nitric acid wastes to recovery concentrated nitric acid that can be reused. The uranium recovery process at the Oak Ridge Y-12 plant generates an overhead condensate stream that is mostly dilute nitric acid, but contains small amounts of fluorides, chlorides, and uranium. The nitrate in this stream is recovered as 30% nitric acid through a distillation process. The waste stream is vaporized through a calcium nitrate-aluminum nitrate trap that removes fluorides and uranium. This trap would also remove most other metal contaminants. The vapor is fed into a distillation column that separates the stream into a nitric acid product and a waste stream that is mostly water with chloride and nitrate contaminants. The column can be designed so that the waste stream meets nitrate discharge permits. This process will probably be useful on waste streams containing up to about 1% impurities.

Calcination is another method of nitrate disposal. Nitrate or ammonium nitrate waste solutions are sprayed into a bed of hot, fluidized sand. The water is evaporated, and the nitrogen compounds are converted to gaseous nitrogen oxides, NO_x. The disadvantage of this process is that a liquid pollutant is merely exchanged for a gaseous one. Increasingly strict EPA limits on gaseous NO_x emissions are likely to make calcination impracticable. Sometimes calcination is made part of an overall recycle process, wherein the NO_x is reabsorbed in water to make nitric acid, which is recycled to the plant. However, fresh concentrated acid is still needed for initial dissolution steps, and the amount of recycle acid (especially if ammonium compounds are also calcined) is much more than the plant can use; thus disposition of the extra nitric acid is still necessary.

A new process with potential application in liquid waste treatment has been developed for chemically reducing NO_x gases.[8,9] The NO_x gases are mixed   R8,9

with a stoichiometric amount of ammonia and reacted on a zeolite catalyst to yield nitrogen gas and water. This process could conceivably be used on liquid nitrate wastes by vaporizing the liquid through the system. However, this application is yet to be demonstrated yet, and the vaporization cost would be substantial.

Ion exchange is occasionally used to remove nitrate from liquid streams. In this case, further treatment is necessary to recycle or dispose of the nitrate absorbed on the ion exchange resin. Occasionally, if the resin is not regenerated, it is simply removed and buried (i.e., a liquid waste is converted to a solid waste). The resin can be regenerated with ammonium hydroxide, producing fertilizer-grade ammonium nitrate. Although other regenerants can be used, they normally introduce other undesirable ions (such as chloride) into the wastewater.

The operator of one fuel fabrication plant, situated near a paper mill with a high-carbon waste are considering a form of biological denitrification. They are experimenting with trucking their nitrate waste to the paper mill, where a biological process consumes the dissolved carbon and reduces the nitrate to nitrogen gas. This is probably not an optimum biological denitrification system because of the transportation necessary and the fact that the paper mill waste does not provide a consistent carbon source for the bacteria. Still, it does show that NFC plants have become aware of the possibilities of biological nitrate removal.

HEAVY-METAL REMOVAL

Aqueous waste streams from nuclear materials processing operations may contain trace quantities of heavy metals, including radionuclides such as uranium (Table 2) which, due to their chemical or radiological properties, can pose a hazard to the environment.

T2

Current discharge levels and disposal regulations for heavy metals

In recent years, much attention has been given to the possible long-term effects of pollutants such as trace heavy metals. The EPA, and a number of state agencies, have set limits on several metals and radionuclides, but the limits are far from being consistent from state to state, or even between plants in one state. Limits for a particular plant often depend on the location of the plant and the ultimate destination of the receiving water. Some examples of NPDES and state metals limits are shown in Table 3.

T3

It is expected that, in the near future, EPA and most state governments will establish more complete lists of limited substances, with stricter release limits.

Current treatment processes

Presently the most common treatment methods for radionuclides and non-radioactive heavy metals involve some combination of settling, storing in lagoons, and outright dumping. Occasionally, ion exchange or evaporation is used.

Table 2. Some reported heavy-metal discharge levels from NFC plants[a]

| Type of plant | Substance | Reported discharge level | |
		Average	Maximum
Fuel fabrication	Chromium	0.03 kg/day	0.2 kg/day
	Nickel	0.06 kg/day	0.11 kg/day
	Copper	0.03 kg/day	0.11 kg/day
Fuel fabrication	Plutonium	< 8.3 dps/m^3	
	Uranium	0.4 g/m^3	1.0 g/m^3
Uranium conversion	Uranium	0.007 g/m^3	1.0 g/m^3
Uranium enrichment	Chromium(VI)	0.02 g/m^3	1.95 g/m^3
	Chromium (total)		0.03 g/m^3

[a]Data are taken from NPDES reports for the NFC plants surveyed.

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Table 3. Typical state limits on metals discharges
from NFC plants

| State	Substance	Limit Average	Limit Maximum	Remarks
Kentucky	Chromium(VI)	$0.05-0.5$ g/m^3 3.41 kg/day	$0.08-1$ g/m^3 6.83 kg/day	Taken from an NPDES permit
	Total chromium	$0.05-0.3$ g/m^3 0.34 kg/day	$0.1-0.5$ g/m^3 0.68 kg/day	
	Zinc	0.5 g/m^3 3.41 kg/day	1.0 g/m^3 6.83 kg/day	
	Copper	0.5 g/m^3 3.41 kg/day	1.0 g/m^3 6.83 kg/day	
North Carolina	Chromium	0.23 kg/day	0.46 kg/day	Taken from an NPDES permit; uranium to be reported but no limit specified
	Nickel	0.23 kg/day	0.46 kg/day	
	Copper	0.45 kg/day	0.95 kg/day	
	Uranium			
Ohio	Arsenic	0.05 g/m^3		Taken from limits for public water supplies outside the plant outfall "mixing zones"
	Barium	1.0 g/m^3		
	Cadmium	0.01 g/m^3		
	Chromium	0.05 g/m^3		
	Copper	1.0 g/m^3		
	Iron	0.3 g/m^3		
	Lead	0.05 g/m^3		
	Manganese	0.05 g/m^3		
	Mercury	0.002 g/m^3		
	Silver	0.05 g/m^3		
	Zinc	5.0 g/m^3		
Oklahoma	Uranium			Reporting required by state but no limits specified
	Radium-226			
	Radium-228			
Virginia	Total chromium	0.1 kg/day	0.2 kg/day	Taken from an NPDES/state permit
	Copper	0.5 kg/day	1.0 kg/day	
	Uranium	0.1 kg/day	0.2 kg/day	
	Cadmium		0.04 g/m^3	
Washington	Chromium		0.2 g/m^3	Taken from an NPDES permit

One common method for treating dissolved metals in wastewater consists of precipitation and settling. Generally, lime is added to increase the pH of the liquid, which precipitates the metals. Settling, sometimes with flocculation, clarifies the liquid and produces a sludge containing most of the metal. The pH of the supernate is then lowered again to a permissible level by adding an acid, such as sulfuric acid. Disadvantages of this method are that a bulky sludge is produced (requiring further handling and disposal), other chemicals are added to the water, and the metal concentrations are not reduced to the low levels that are required (<1 g/m^3).

In many cases, where an effluent is considered to be too difficult or too radioactive to treat, it is simply stored in lagoons or ponds for indefinite periods of time. This is done especially with uranium mill tailings and tailing leach effluents, and with wastes from conversion plants that use nitric acid solvent extraction processes. Disadvantages of lagoons are the continuing need for more lagoon construction, storage rather than elimination of the waste, and possibilities of seepage from the lagoon.

Ion exchange is sometimes used to remove metals from wastewater. The disadvantages of ion exchange are regeneration (or disposal of resin if regeneration is not done) and the addition of another ion, usually chloride, to the water. Evaporation is used to concentrate waste liquids in certain cases, but evaporators are expensive and use a large amount of heat energy.

Another processing method which may be considered is the sorption or complexation of dissolved metal species by microorganisms:

$$M_{dissolved} + cells \rightarrow (M \cdot cells)_{insoluble\ complex} \ \text{②}$$
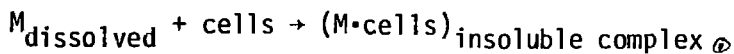
Solid-phase (biomass) concentration of 10 to 20 wt % can be attained.[10] A number of investigators have indicated that microbially synthesized polymers

extending from the outer membrane of a cell are responsible for the binding of metal ions from solution.[11] Metal cations may be complexed by negatively charged sugar units at the end of a polysaccharide chain or by chelation through negatively charged oxygen atoms (Fig. 2). Rothstein and co-workers have cited evidence that exocellular polyphosphate groups, associated with sugar metabolism, are responsible for the binding of uranium (uranyl ion) from aqueous solution.[12]

R11

F2

R12

EXPERIMENTAL RESULTS

High-rate, biological denitrification has been experimentally demonstrated using engineering-scale fluidized-bed systems treating authentic nitrate wastes from the nuclear fuel cycle. Biological removal and concentration of heavy metals has been verified in bench-scale equipment both batchwise and in continuous contactors.

Denitrification

Biological denitrification, as referred to in this paper, is the biological reduction of nitrate or nitrate to gaseous molecular nitrogen.[13] It commonly takes place in soil under anaerobic conditions by the various strains of facultative anaerobic bacteria which are responsible for recycling nitrogen compounds back to the atmospheric molecular nitrogen pool.[14] The reaction requires a carbon source which has been successfully supplied in the form of various alcohols and acetates. The rate of denitrification is dependent upon the type of carbon substrate supplied as well as upon other operating parameters such as the pH and temperature of the system. With ethanol as the carbon source, the reaction may be written in unbalanced form as:

R13

$$3NO_3^- + 2C_2H_5OH \rightarrow CO_2 + N_2 + H_2O + OH^- + X\ C_5H_7O_2N.$$
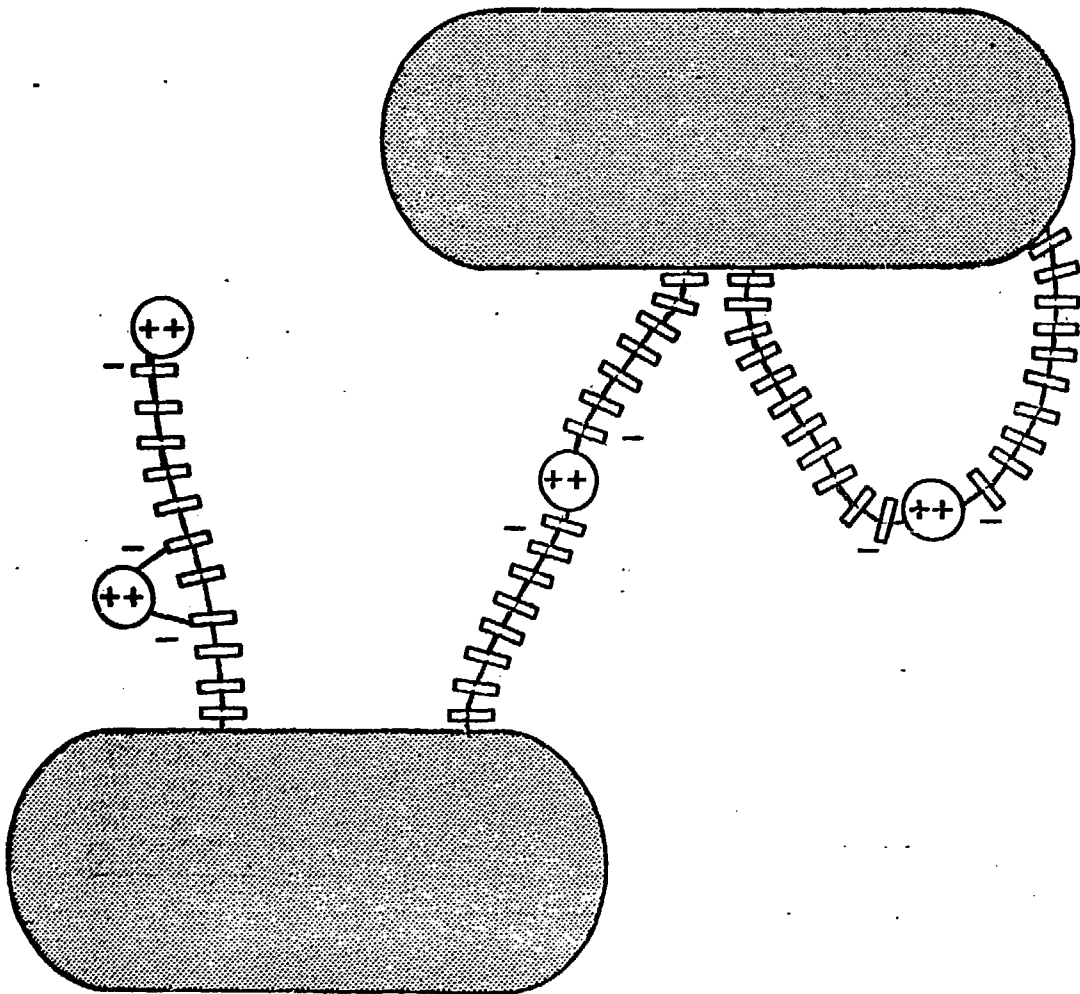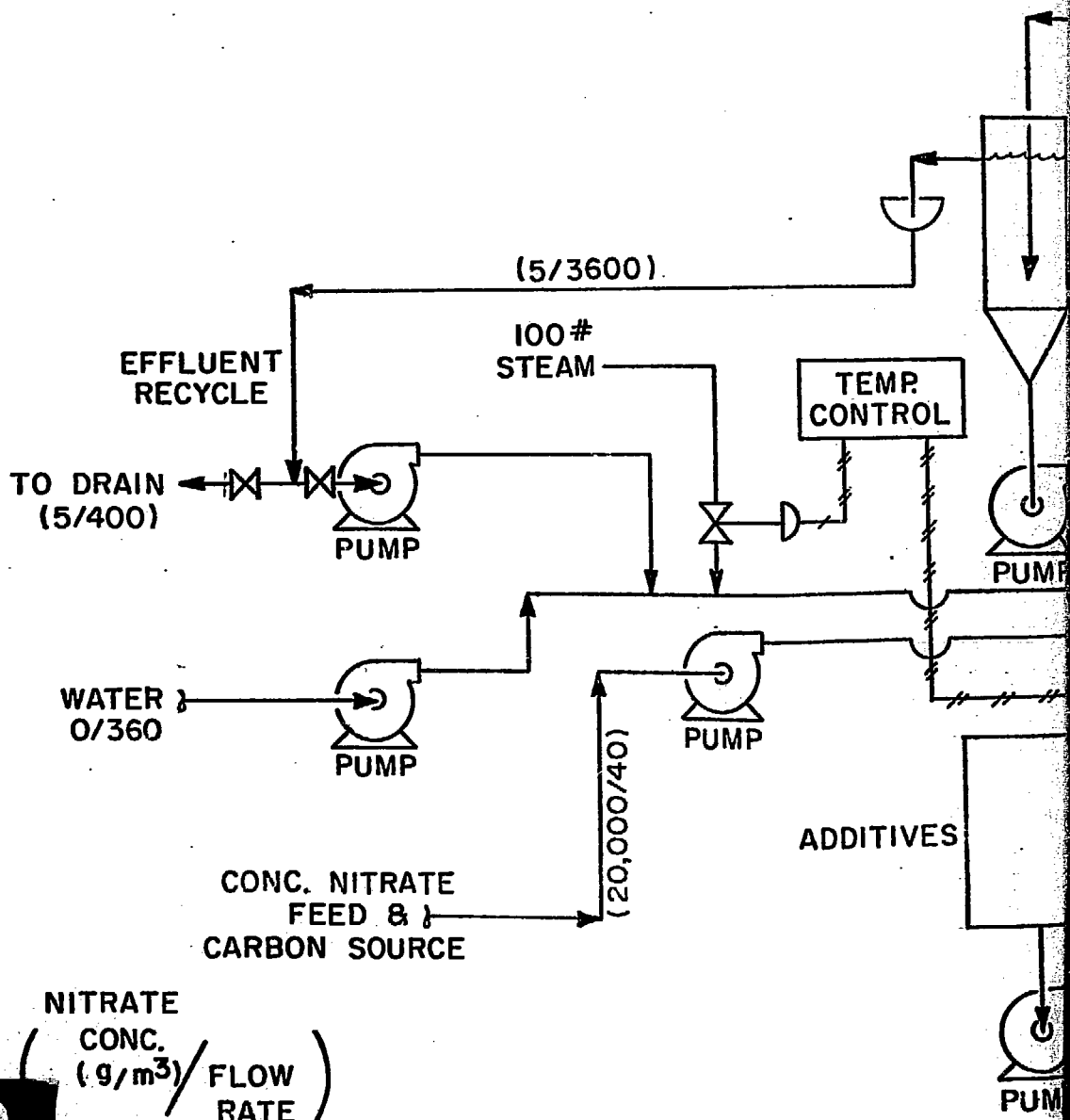
Fig. 8
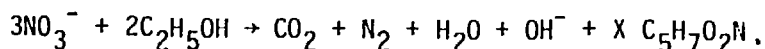
ORNL DWG 78-5294

Figure 2. SCHEMATIC OF POTENTIAL INTERACTION OF URANIUM IONS WITH NEGATIVELY CHARGED SURFACE COMPONENTS OF MICROBIAL CELL.

The chemical equation coefficients on nitrate and ethanol reflect the observation that the ratio of carbon consumed to nitrogen (as nitrate) reacted is about 1.3 to 1.5 mole/mole. The composition of the biomass may be given approximately as $C_5H_7O_2N$. The biomass yield is roughly 0.1 g/g of nitrate consumed.

At the Oak Ridge National Laboratory, high-rate denitrification processes are being developed which utilize denitrifying bacteria adhering to particles of anthracite coal or sand. The particles, with adhering bacteria, are fluidized by flow of the aqueous stream being treated as it passes upward through a columnar bioreactor.[15] Two column geometries have been studied: tapered (inverted, truncated cone), and cylindrical with a tapered top section. The tapered geometry permits operation over a greater range of flow rates than with a cylindrical geometry alone.

One of the fluidized-bed bioreactors tested is shown in Figure 3. The reactor consists of a cylindrical section of 51 mm in diam by 3.7 m long beneath a tapered 51-mm to 76-mm diam by 0.6-m long solids disengaging zone. Sampling ports were located at 0.6-m intervals. With a sufficient population of denitrifying bacteria established on a fluidized bed, performance was evaluated using both ammonium nitrate and raffinate waste as feed and ethanol as the carbon source. The feed carbon/nitrate-nitrogen ratio (C/N) was maintained between 1.8 and 2.0. Typically the carbon utilized was 1.2 times the nitrogen converted. A typical set of concentration profiles for nitrate, nitrite, and carbon (as ethanol) is shown in Figure 4.

The empty reactor volume of fluidized-bed systems studied ranged from 2 to 240 liters. Feed nitrate concentrations ranging from 100 to 7500 g/m^3 were treated, achieving denitrification rates as high as 75 kg/day-m^3. Effluent
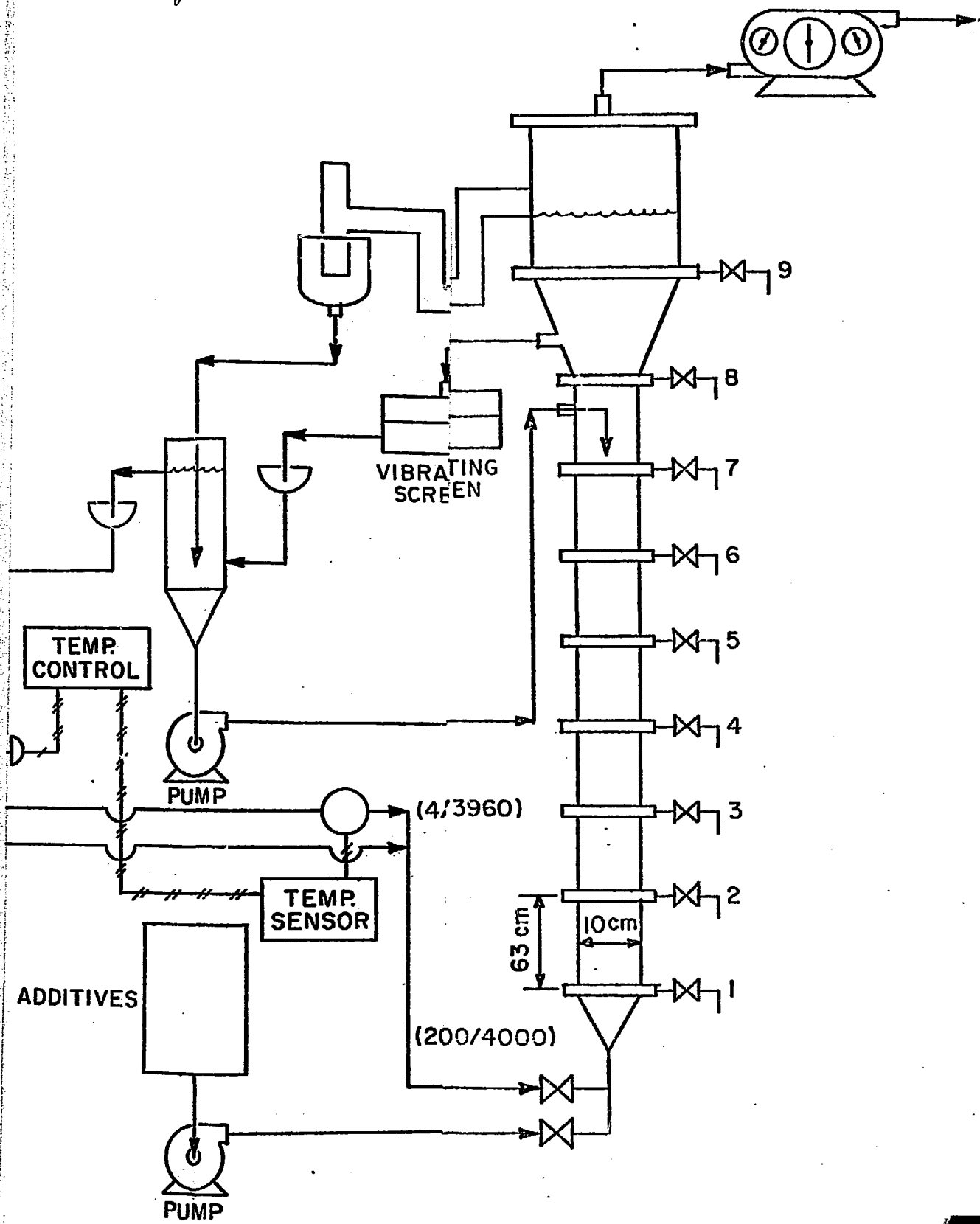
Fig. 3

(5/3600)

EFFLUENT
RECYCLE

100#
STEAM

TEMP.
CONTROL

TO DRAIN ◄─┤╳├──┤╳├─
(5/400)

PUMP

PUMP

WATER }
0/360

PUMP

PUMP

(20,000/40)

CONC. NITRATE
FEED &
CARBON SOURCE

ADDITIVES

$\left(\dfrac{\text{NITRATE CONC.} \, (\text{g/m}^3)}{\text{FLOW RATE} \, \text{cm}^3/\text{min}} \right)$

PUM

10 cm Dia x 5m FLUIDIZED BED

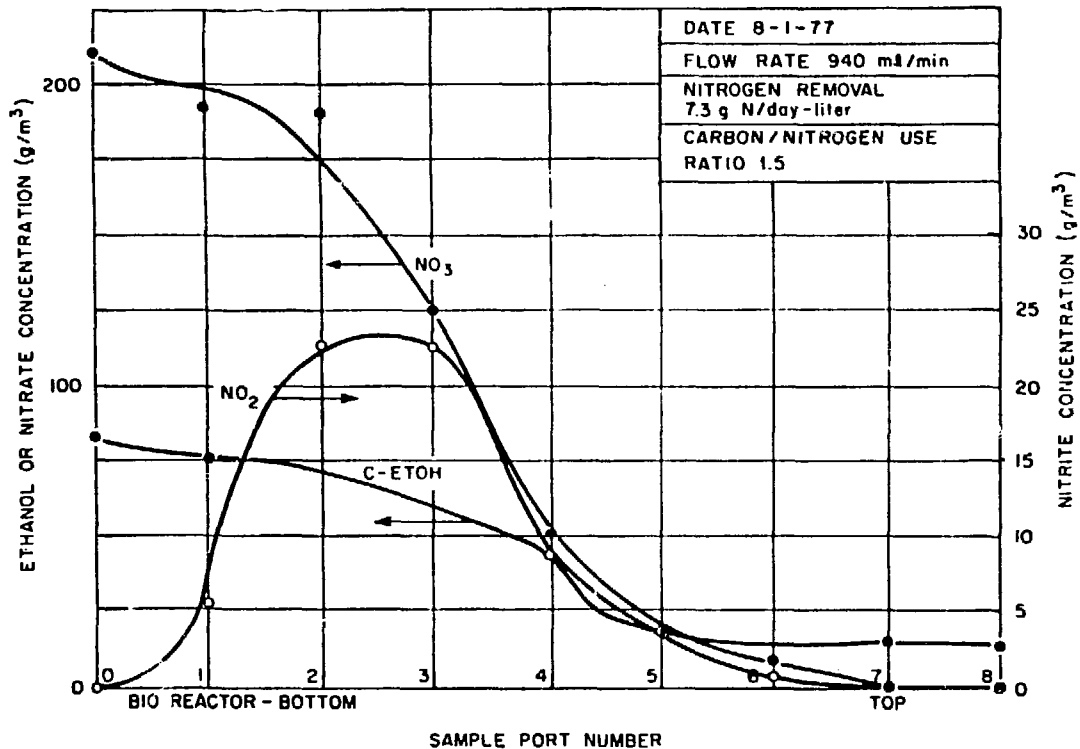Fig. 3   ORNL-DWG 78-5058

UIDIZED BED BIOREACTOR-90% RECYCLE TEST

ORNL-DWG 77-1890R2

Fig. 4. Concentration profiles of nitrate, nitrite, and carbon (as ethanol).

concentrations less than 1 g/m^3 was demonstrated. These results are summarized by the curve in Figure 5.

F5

Heavy-Metal Removal

Since the literature is replete with examples of metal uptake from aqueous solution by microorganisms, six microbial strains were surveyed to determine if significant differences existed between species with regard to uranium isolation. The survey showed that species differences were quite pronounced (Table 4) and three cultures were selected for more detailed study.

T4

Pure strains of Saccharomyces cerevisiae (a yeast), Psudomonas aeruginosa (a bacterium), and the mixed culture of denitrifying bacteria were tested to determine the effect of initial uranium concentration, hydrogen ion concentration, and temperature on the rate of uranium accumulation by cells in a single, well-mixed contacting stage. All three parameters affected the rate of uranium accumulation, but had little effect on the equilibrium distribution coefficient in the range of parameter values studied. For a given set of conditions, the rate was strongly influenced by species differences (Figure 6). For all three cultures, uranium accumulation by washed, resuspended cells was rapid, and a high degree of uranium removal from solution was achieved. As an example, using the denitrifying bacteria (cell concentration = 1900 g/m^3; dry basis) the soluble uranium concentration was reduced from 10 g/m^3 to 0.5 g/m^3 in a 60-min contact time, obtaining distribution coefficients of approximately 17,000.

In a parallel study, thin sections of yeast cells which had been contacted with a uranyl nitrate solution were examined by electron microscopy (Figure 7). The bound uranium appeared as a fibrillar material on the exterior of the cells. Energy dispersive X-ray spectra confirmed that little, if any, uranium
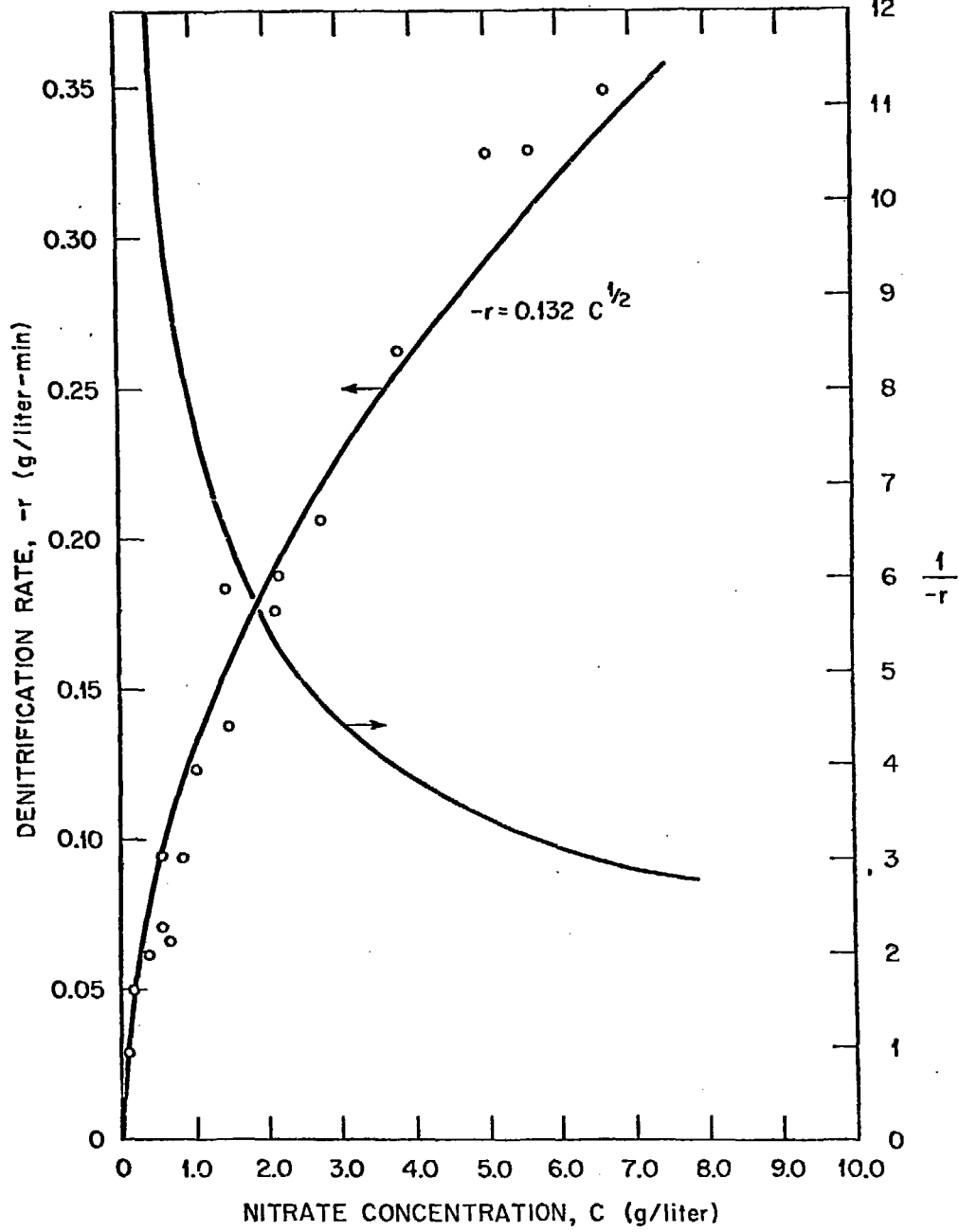
$-r = 0.132\ C^{1/2}$

DENITRIFICATION RATE, $-r$ (g/liter-min)

$\dfrac{1}{-r}$

NITRATE CONCENTRATION, C (g/liter)

Fig. 5

Table 4.

Isolation of uranium from solution by microorganisms
during resuspended contact. Initial uranium concentration
was 20 mg/liter. Temperature was 25°C.

Microorganism	Removal (%)	Cell concentration, (dry basis) (g/liter)	Metal distribution[a] coefficient
Pseudomonas aeruginosa (Bacterium)	92	1.2	9,600
Zoogloea ramigera (Bacterium)	72	1.0	2,730
Paecilomyces marquandii (Fungus)	94	1.2	13,100
Penicillium chrysogenum (Fungus)	97	3.1	10,300
Ashbya gossypii (Yeast)	73	7.0	390
Saccharomyces cerevisiae (Yeast)	95	1.3	15,000

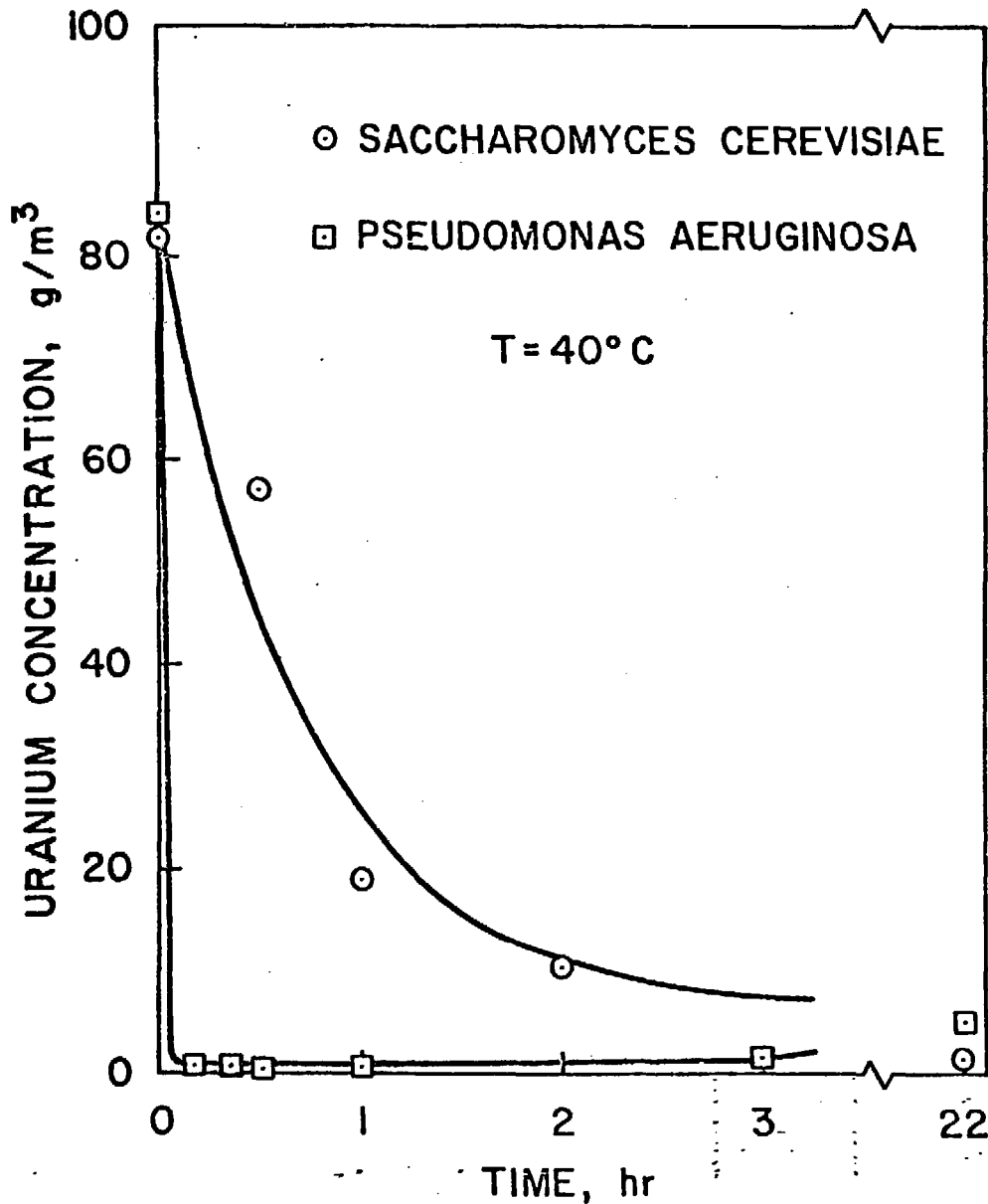[a]Metal distribution coefficient = $\dfrac{\text{g metal/g cells (dry)}}{\text{g metal/g solvent}}$

ORNL DWG 78-578
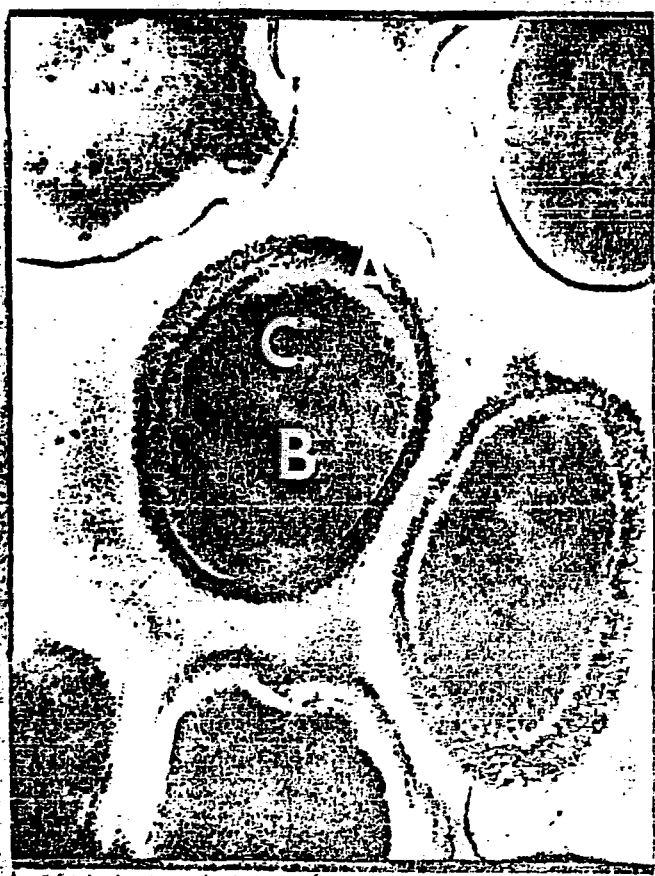

Figure 6. REMOVAL OF URANIUM FROM AQUEOUS SOLUTION BY WASHED RESUSPENDED CELLS OF
SACCHAROMYCES CEREVISIAE AND PSEUDOMONAS AERUGINOSA.

Figure 7. ELECTRON MICROGRAPH OF
SACCHAROMYCES CEREVISIAE
CELL WHICH HAS BEEN EXPOSED
TO URANIUM

Figure 7.

was taken into the cells. Thus the hypothesis that certain metal species can be removed from solution and collected by microbial cells through surface interactions appeared to be well founded.

The denitrifying bacteria were then tested for effectiveness in removing uranium from a solvent extraction raffinate waste solution obtained from the Goodyear Atomic Gaseous Diffusion Plant in Portsmouth, Ohio. Adjustment of solution pH to 4 followed by cell contact and centrifugation lowered the uranium concentration from 4 g/m^3 to < 0.02 g/m^3. Adjustment of pH to 8 resulted in reduction of other metals of interest (Al, Fe, Cu, Cr) to low solution concentrations (e.g., Fe from 7340 to 2 g/m^3) (Table 5). Similar results were obtained with the raffinate waste supplemented with uranium for an initial soluble concentration of 100 g/m^3 (Table 6). On the basis of this information, a preliminary processing strategy was developed for aqueous waste streams which contain both nitrate and dissolved heavy metals (e.g., uranium). The conceptual process design consists of two primary unit operations--a bioreactor (which generates a "biosorbent" as a by-product of the nitrate conversion reaction) and a contactor (for removal of dissolved heavy metals by the "biosorbent"). The "biosorbent", excess cells from the denitrification bioreactor, is cycled to the contactor located upstream of the bioreactor in the flowsheet. Thus, the presence of possible growth-inhibiting heavy-metal constituents in the waste stream would not interfere with bioreactor performance, and the ability to use different process conditions for the two unit operations yields a more favorable overall process performance.

Several contactor designs for continuous heavy-metal removal have been tested, and a countercurrent contacting column has proved quite effective. By continuously feeding denitrifying bacteria grown on coal particles in the fluidized-bed denitrification bioreactor to the top and pumping a solution

Table 5. Isolation of uranium and other metals from a solvent
extraction raffinate waste solution[a] by chemical precipitation
and sorption by denitrifying bacteria in a
batch contactor

Metal	Adjusted pH	Metal concentration in solution, g/m^3		
		Before adj.	After adj.	After cell contact
U	1	4.0	3.3	2.7
	4	4.0	0.18	(<0.02)
	8	4.0	(<0.02)	(<0.02)
Al	1	7340	5000	4500
	4	7340	164	300
	8	7340	2.9	1.7
Fe	1	1840	1440	1150
	4	1840	1.1	0.9
	8	1840	1.0	0.8
Cu	1	263	206	190
	4	263	61	71
	8	263	0.3	0.5
Cr	1	41	34	30
	4	41	0.6	0.6
	8	41	0.6	0.5

[a]Obtained from Goodyear Atomic Gaseous Diffusion Plant, Portsmouth, Ohio.

Table 6. Isolation of uranium and other metals from
a solvent extraction raffinate waste solution[a]
supplemented with uranium by chemical precipitation
and sorption by denitrifying bacteria in a batch
contactor

Metal	Adjusted pH	Metal concentration in solution, q/m^3 [b]			
		Before adj.	After adj.	Contact solution[c]	After cell contact
U	1	100.3	80.3	72.4	62.0
	4	100.3	19.0	17.1	3.5
	8	100.3	0.1	0.09	<0.1
Al	1	7360	5120	4608	4500
	4	7360	821	738.9	712
	8	7360	3.6	3.2	<1
Fe	1	1770	1170	1053	705
	4	1770	19	17.1	3.7
	8	1770	1.2	1.1	0.6
Cu	1	258	207	186.3	(61,127,186)
	4	258	127	114.3	(36,111,36)
	8	258	<1	<1	<1
Cr	1	38	30	27	(25,24,67)
	4	38	2.4	2.2	2.1
	8	38	0.6	0.54	0.6

[a]Obtained from Goodyear Atomic Gaseous Diffusion Plant, Portsmouth, Ohio.

[b]Average on three determinations.

[c]Based on dilution by addition of 10-ml cells.

containing 25 g/m^3 uranium up through the column, an effluent uranium con-
centration of $\sim$0.5 g/m^3 was obtained with a liquid residence time of only
$\sim$8 min (Figure 8).

PROCESS COMPARISON

Using the engineering-scale results, design criteria for a full-scale
bioprocessing system to reduce the concentrations of nitrate and radioactive
contaminants in the solvent raffinate streams at the Portsmouth Gaseous
Diffusion Plant to releasable levels were established and the capabilities
and economics of bioprocesses compared with other potential waste treatment
methods for the processing of these specific waste streams.

Staff members at the Portsmouth Gaseous Diffusion Plant provided a
description of the three specific nitrate waste streams which will require
treatment to meet future effluent standards.

These very acidic waste streams, denoted A, B, and C, are composed of
raffinate wastes from the solvent extraction processes; and A and B streams
are very similar in composition. The flow rate for the combined A and B
raffinate is 1600 gal/month (0.14 liter/min), while the C raffinate contributes
1000 gal/month (0.09 liter/min). As can be seen in Table 7, the waste liquids
contain a high concentration of nitrate and large quantities of dissolved
solids, which tend to complicate treatment processes.

Discharge Standards

The discharge standards that will be in force during the process opera-
tion are most important since these will represent an important design
criteria. Estimates of future discharge limits are made by careful examina-
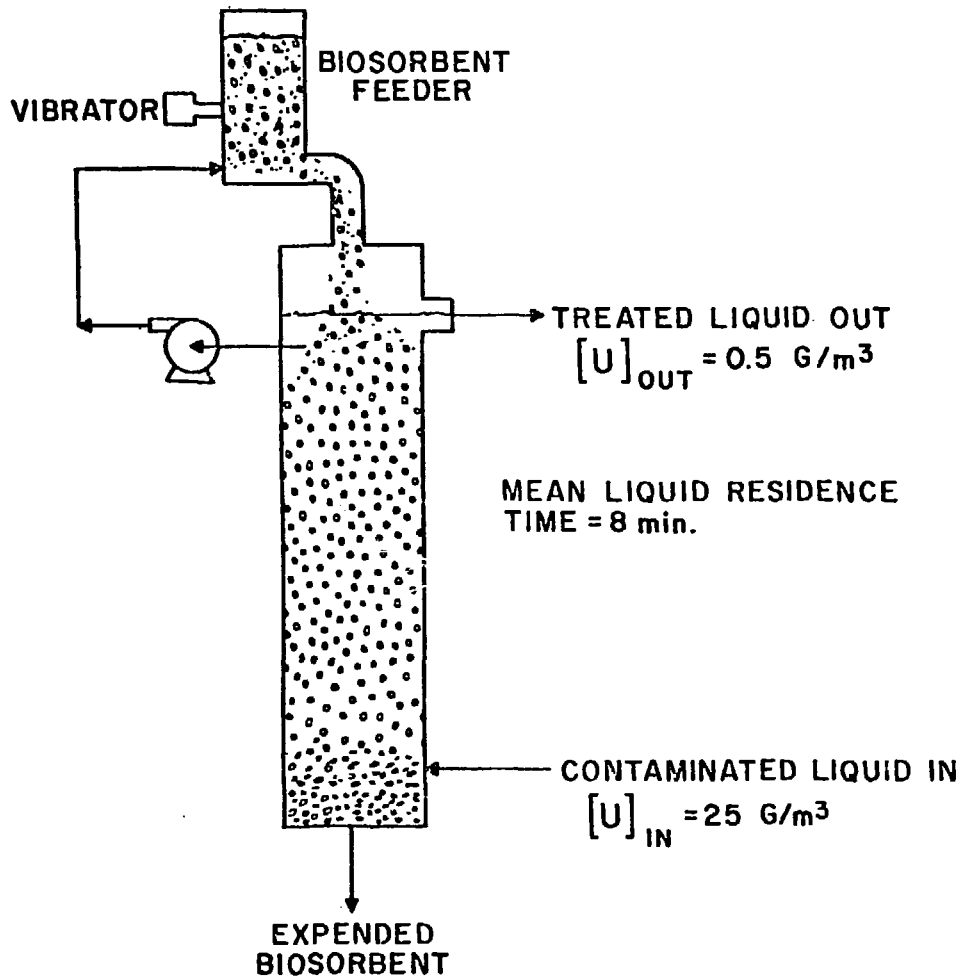tion of present limits and anticipation of trends toward more stringent limits.

Fig. 8. Continuous countercurrent contactor for removal of heavy metals.

Table 7. Analysis of raffinate samples[a,b]

Component	Concentration (wt % in dissolved solids)	
	A and B raffinate	C raffinate
Aluminum	>10	10
Calcium	0.6	0.6
Chromium (total)	0.2	0.008
Copper	1	1
Iron	1	10
Magnesium	0.03	0.8
Manganese	0.003	0.02
Molybdenum	0.006	0.01
Sodium	>10	1
Nickel	0.06	0.3
Lead	N.D.[c]	0.02
Silicon	0.1	0.03
Tin	0.001	0.03
Titanium	0.008	0.02
Vanadium	0.001	0.003
	Concentration (in liquid)	
Fluoride,[d] g/m^3	20,000	16,000
Nitrate,[d] %	28-30	44-45
Uranium,[d] g/m^3	0.6	25.3
Dissolved solids, g/m^3	196,000	196,000
Ammonium,[d] g/m^3	3.5	3.8

[a]Data by courtesy of the staff of Portsmouth Gaseous Diffusion Plant.
[b]Based on a single sample.
[c]N.D. = not detected.
[d]The concentrations of these species were not corrected for solution density.

Table 8 shows the existing discharge limits set by the state of Ohio for

water that, with conventional drinking water purification treatment, will be

suitable for human intake. The present discharge limits that would apply

to the effluent from this waste process, if it were now operational, are

given in Table 9. The information in Table 9 is taken from the current

discharge permit for the Portsmouth Gaseous Diffusion Plant. The authors'

estimates of future discharge limits of interest in this study are given in

Table 10. In most cases, the estimated 1983 limits are approximately one-

half those presently in force and will be used for design purposes. It should

be noted that Portsmouth currently utilizes a significant dilution of the

raffinate waste stream with other process-derived water to help meet current

standards.

Criteria for Process Evaluation

Dilution of the effluent before discharge may be possible to some extent

in the future; therefore, two cases are considered in this design study. A

dilution factor of 2300:1 was assumed in Case I, as suggested by the Ports-

mouth staff, while a more nominal dilution factor of 530:1 was allowed in Case

II. No gaseous pollutants such as NO_x will be emitted from the process.

Upsets due to feed conditions and process malfunctions will be controlled

by redundant equipment and recycle to holding tanks.

Process Flowsheets

With the criteria for the design of the waste treatment facility

established, flowsheets were developed for the processing of the Portsmouth

raffinate waste streams utilizing both biological and nonbiological processes.

Three nitrate removal processes consisting of ion exchange, sugar denitrifi-

cation, and biodenitrification were studied. Similarly, three methods of

Table 8. Ohio limits on discharge[a]

Component	Limit (g/m^3)	Remarks
Nitrate – N	10	
Chloride	250	
Arsenic	0.05	
Barium	1.0	
Cadmium	0.01	Taken from limits for public water supplies outside the plant outfall "mixing zones"
Chromium	0.05	
Copper	1.0	
Iron	0.3	
Lead	0.05	
Manganese	0.05	
Mercury	0.002	
Silver	0.05	
Zinc	5.0	

Dissolved solids

May exceed one but not both of the following:

(a) 500 g/m^3 as a monthly average nor exceed 750 g/m^3 at any time (equivalent 25°C specific conductance values are 800 and 1200 micromhos/cm), or

(b) 150 g/m^3 attributable to human activities (equivalent 25°C specific conductance value is 240 micromhos/cm).

[a]Source: Ohio EPA, Water Quality Standards, Chap. 3745 * 1 of the Administrative Code, pp. 36-37 (Dec. 30, 1977).

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Table 9. Present discharge limits for the Portsmouth Plant[a]
(Effective July 1, 1977–April 15, 1980)

'Effluent characteristic	Discharge limitations	
	Daily average (g/m^3)	Daily maximum (g/m^3)
Flow (MGD)[b]	4.5[c]	5.0[c]
Dissolved solids	1000	1500
Suspended solids	20	30
Fluoride	1.0	1.5
Chromium (6+)	0.05	0.1
Zinc	0.5	1.0
Nitrate (N)	10	20

[a]Source: Portsmouth Gaseous Diffusion Plant current Permit
OH0006092, p. 2.

[b]MGD = million gallons/day.

[c]For normal operating conditions does not include high storm water flows.

Note: The pH shall not be less than 6.0 nor greater than 9.0. There shall be no discharge of floating solids or visible foam in other than trace amounts. Samples taken in compliance with the monitoring requirements specified above shall be taken prior to mixing with the water in Little Beaver Creek.

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Table 10. Authors' estimate of future (1983) discharge limits for the Portsmouth Gaseous Diffusion Plant

Effluent characteristic	Discharge limits, daily average (g/m^3)
Nitrate-N	5.0
Uranium	< 1.0[a]
Dissolved solids	500

[a]Calculation from current 10 CFR 50 standard, assuming all uranium is ^{235}U would result in an effluent limit of 4.7 g/m^3.

heavy-metal removal--ion exchange, flocculation, and a bioprocess--were studied.
Since the raffinate waste streams to be treated contained both nitrate and
trace metals such as uranium, a complete flowsheet for the process would
include a nitrate removal step as well as a heavy-metal removal step and the
necessary pre-processing steps.

Nine flowsheets were developed in order to compare the processes and to
evaluate each in conjunction with the other steps of the treatment scheme.
These flowsheets, which consisted of all combinations of the three processes
for the two steps of treatment, are identified by the following matrix:

Trace metal \ Nitrate removal	Sugar denitrification	Ion exchange denitrification	Bio-denitrification
Flocculation	I	VI	VII
Ion exchange	II	IV	VIII
Bioprocess	III	V	IX

In the flowsheets utilizing sugar denitrification, the denitrification
step precedes the heavy-metal removal step. In all other flowsheets, the
denitrification step follows the heavy-metal removal step. It was necessary
to include a NO_x catalytic decomposition step in those flowsheets involving
sugar denitrification in order to avoid emission of concentrated NO_x.

Flowsheet Evaluations

The equipment necessary to accomplish the processing steps described
in the nine flowsheets was estimated using the established criteria. Overall
and component material balances on each flowsheet provided the quantity and
composition of the discharge streams from each treatment scheme. In these
calculations, it was assumed that upset conditions could be controlled with
recycle to holdup tanks within the system.

The results of the calculations are given in Tables 11 and 12. Table 11 represents effluent concentrations for Case I, in which a dilution factor of 2300:1 is allowed prior to discharge to the river. Such a dilution factor may be possible in the Portsmouth facility, but it does not represent the general case. No dilution of the processed waste is allowed in Case II (Table 12) other than that required for achieving the total dissolved solids limits. To achieve this end, a dilution of 530:1 was established.

A sludge stream which requires disposal is generated in each flowsheet. Since this stream has approximately the same magnitude in each flowsheet, no evaluation of it was made in the comparison of the flowsheets.

As can be seen from Table 11, all flowsheets successfully meet the uranium discharge limit.

For nitrate removal, flowsheets involving the ion exchange processes were not successful in meeting the nitrate discharge limit. In this method, nitrate ions are exchanged for chloride ions in the effluent stream; thus, the effluent does not meet discharge limits for chloride unless the effluent stream is diluted. Additionally, the regeneration of the ion exchange medium produces a concentrated stream of ammonium nitrate which has a flow rate equal to about 75% of the main effluent stream. Thus, an entirely new waste water treatment stream is created that must be treated. The excessive volume of the regeneration stream precludes burial of the waste; therefore, the stream must eventually be discharged to the river. The net effect of the ion exchange method for nitrate removal is to generate an additional chloride pollutant

Table 14. Discharges in Flowsheets I-IX (Case I)

Component discharged	Portsmouth present standard	Estimated 1983 limit	Initial feed	Discharges in respective flowsheet after dilution of 2300:1								
				I	II	III	IV	V	VI	VII	VIII	IX
Nitrate-N, g/m^3	10	5.0	79,000	4	4	4	34^a	34^a	34^a	4	4	4
Uranium, mg/m^3 [b]	4.7^c g/m^3	< 1.0 g/m^3	10.0 g/m^3	0.43	0.43	0.43	0.43	0.43	0.43	0.43	0.43	0.43
Dissolved solids, g/m^3	1000	500	$190,000^d$	18^e	22^e	18^e	130^f	130^f	130^f	110^g	110^g	110^g
Flow rate, gal/day			87	200,000	200,000	200,000	200,000	200,000	200,000	200,000	200,000	200,000
Sludge by-product for disposal, gal/day (burial)				8.7	9.2	9.0	8.7	9.2	9.0	8.7	9.2	9.2

[a] Regeneration stream included.

[b] Except where noted as g/m^3.

[c] Calculation from current 10 CFR 50 Standard assuming all uranium is ^{235}U.

[d] Majority dissolved metals.

[e] Majority $NaNO_3$.

[f] Majority $NaCl$ and NH_4NO_3.

[g] Majority Na_2CO_3.

Table 12. Discharges in Flowsheets I-IX (Case II)

Component discharged	Portsmouth present standard	Estimated 1983 limit	Initial feed	Discharges in respective flowsheet after dilution of 530:1								
				I	II	III	IV	V	VI	VII	VIII	IX
Nitrate-N, g/m^3	10	5	79,000	13	13	13	150[a]	150[a]	150[a]	0.06	0.06	0.06
Uranium, mg/m^{3b}	4.7[c] g/m^3	< 1.0 g/m^3	10 g/m^3	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Dissolved solids, g/m^3	1000	500	190,000[d]	80[e]	100[e]	80[e]	1000[f]	1000[f]	1000[f]	500[g]	500[g]	500[g]
Flow rate, gal/day			87	46,000	46,000	46,000	46,000	46,000	46,000	46,000	46,000	46,000
Sludge by-product for disposal, gal/day (burial)				8.7	9.2	9.0	9.0	9.0	8.7	8.7	8.7	9.0

[a]Regeneration stream included.

[b]Except where noted as g/m^3.

[c]Calculation from current 10 CFR 50 Standard assuming all uranium is ^{235}U.

[d]Majority dissolved metals.

[e]Majority NaNO$_3$.

[f]Majority NaCl and NH$_4$NO$_3$.

[g]Majority Na$_2$CO$_3$.

while achieving no reduction in the total amount of nitrate discharged to the river. Because the ion exchange method for nitrate removal was unacceptable, Flowsheets IV, V, and VI were not considered in further evaluation of the processes.

The estimate using Case II criteria, where only process dilution was allowed, generated the effluent streams described in Table 11. In this case, a dilution factor of 530:1 was used. The biodenitrification flowsheets are the only ones which meet the nitrate discharge limits for this case without additional dilution. In the flowsheets utilizing sugar denitrification, an additional dilution factor of 3 would be required to meet the limiting nitrate standard. Although all of the flowsheets require some dilution for meeting total solids limits, the flexibility of the biodenitrification process is clearly illustrated.

Cost Estimates

Estimates of the costs of equipment required for Flowsheets I, II, III, VII, VIII, and IX were prepared in order to economically evaluate the proposed processes. Equipment flowsheets were developed for use in the economic evaluation, and equipment items which were redundant were not included in the cost estimate.

The cost data presented were obtained from pertinent handbooks and vendor quotes.[16] In cases where an escalation index was needed, the Marshall and Stevens Equipment Cost Index was used. R 16

The installed equipment costs were converted to a $/gal feed basis. For this conversion, the equipment was assumed to have a 7-year life and capital was assumed to be available at 7% interest compounded annually, but taxation was not considered. In addition to the equipment cost estimate, estimates of

the chemical, service, and operating manpower costs were prepared. These estimates for Cases I and II are presented in Tables 13 and 14, respectively.

The biological processes were very competitive economically with all the other processes and, in fact, the process with minimum cost must include biological denitrification. There is less than 30% difference in the total processing costs for all the flowsheets considered in Case I (2300:1 dilution), as shown in Table 13. This difference is small in light of the potential error associated with this type of preliminary cost estimate. However, the cost of processing with Flowsheet III is significantly higher than the other processing schemes; therefore, it should probably be considered uneconomical. Operating manpower cost is the major variable, constituting between 70 and 80% of the total processing cost. Since only limited data are available on the operational aspects of some of the advanced systems, necessarily conservative estimates were made, thus potentially penalizing these processes unnecessarily. This would include all of the bioprocesses.

Although it was necessary to employ somewhat larger biodenitrification reactors in order to meet the criteria set for nitrate discharge in Case II (530:1 dilution), the comparison of the installed costs for the flowsheets involving biodenitrification between Case I and Case II shows that only a small amount of additional capital is required. The flowsheets utilizing the biodenitrification process were able to meet the nitrate limit set in Case II (530:1 dilution) with only a 3% increase in the total processing cost. The three flowsheets that could meet the release limits for Case II had unit costs that were very similar and are well within estimation errors. All of these processes utilized biodenitrification coupled either with flocculation, ion exchange, or bioprocess for uranium removal. In the case

Table 13. Total cost of processing waste for Case I
(Dilution factor, 2300:1)

Type of costs	Flowsheet					
	I	II	III	VII	VIII	IX
Chemical, $/gal feed	0.30	0.29	0.29	0.46	0.46	0.46
Service, $/gal feed	0.069	0.069	0.072	0.020	0.024	0.021
Operating manpower, $/gal feed	3.7	3.4	4.4	3.4	3.4	3.7
Installed equipment[a] $/gal feed	0.99	1.1	1.2	0.79	1.0	0.93
Total processing cost, $/gal feed	5.1	4.9	6.0	4.7	4.9	5.1

[a]Calculated assuming (1) 7-year equipment life, (2) 7% interest compounded annually, and (3) no taxation.

Table 14. Total cost of processing waste for Case II
(Process dilution only)

Type of cost	Flowsheet		
	VII	VIII	IX
Chemical, $/gal raw waste	0.49	0.49	0.49
Service, $/gal raw waste	0.02	0.02	0.02
Operating manpower, $/gal raw waste	3.40	3.40	3.40
Installed equipment,[a] $/gal feed	0.88	1.10	1.00
Total processing cost, $/gal feed	4.79	5.01	4.91

[a]Calculated assuming (1) 7-year equipment life, (2) 7% interest compounded annually, and (3) no taxation.

Comparison of the installed costs for the flowsheets involving biodenitrification between Case I (2300:1 dilution) and Case II (530:1 dilution) shows that only a small amount of additional capital is required. The flowsheets utilizing the biodenitrification process were able to meet the nitrate limit set in Case II (530:1 dilution) with only a 3% increase in the total processing cost, while the sugar denitrification was unsuccessful in this regard. The three flowsheets that

of the Portsmouth raffinate streams, the uranium removal requirement is such
a small part of the overall problem that it is difficult to effectively
compare uranium removal techniques.

Discussion

The biological processes are competitive with other potential
technologies for the removal of nitrate and radioactive contaminants
from the Portsmouth Gaseous Diffusion Plant's solvent extraction
raffinate waste streams and, under some criteria, represent the only
possible processing choice. The biological processes are competitive
on both cost and rescheduling bases. If future discharge limits approach
the Case II (dilution limited to 530:1) criteria, then the biodenitri-
fication process is the only one able to meet these criteria for nitrate
removal.

The uranium level in the Portsmouth Gaseous Diffusion Plant's solvent
extraction raffinate waste stream is too low for an objective evaluation
of the various heavy-metal removal processes. This is evidenced by the
fact that the three processes studied--flocculation, ion exchange, and
bioprocess--were all able to meet the uranium discharge criteria. At
Portsmouth, the uranium removal aspect is a very minor problem and all the
heavy-metal removal schemes are essentially economically equivalent. At
other points in the fuel cycle (i.e., a fuel fabrication plant such as the
one at Erwin, Tennessee, where the uranium concentration is high and
appreciable uranium is to be recovered from the waste), the biological
process for heavy-metal removal would be favored since uranium recovery
from the sludge would be very simple. However, the Portsmouth application
of biological heavy-metal removal would be a good proving ground for this
process even though it would be even more effectively used at other sites.

Conclusions

By comparing the bioprocesses with other possible technologies for nitrate and heavy-metal removal from the Portsmouth Gaseous Diffusion Plant's solvent extraction raffinate waste streams, several conclusions can be drawn:

1. Only the sugar denitrification and the biodenitrification processes are effective for nitrate removal under present discharge limits. Ion exchange is ineffective since it merely changes the chemical form without removing the nitrate.

2. The biodenitrification process is capable of removing nitrate to less than 1 g/m^3. The sugar denitrification process is not effective for removing nitrate below about 0.5 $\underline{N}$.

3. All of the processes evaluated for uranium removal are adequate due to the small reduction needed to meet both the present and future postulated discharge limits. The Portsmouth facility would be a good proving ground for the biological heavy-metal process, even though it would be even more effectively utilized in treatment of a more-concentrated waste stream.

4. Variation in the total processing costs among all the flowsheets for Case I (2300:1 dilution factor) is only about 30%. The flocculation heavy-metal removal — biodenitrification flowsheet is slightly more economical than the other schemes; however, the heavy-metal processes are essentially equivalent in this application. For all Case I flowsheets the major cost variable is the operating manpower, which contributed 70-80% of the total processing costs.

5. **The biodenitrification process is the only process that will meet the Case II (minimum dilution) criteria for a modest increase in processing cost estimated at about 3% over the Case I criteria.**

6. .The results of this preliminary evaluation indicate that it would be appropriate to proceed with the pilot facility demonstration of the bioprocesses at Portsmouth.

PILOT-PLANT DESIGN

As a result of these positive results, a denitrification pilot plant is being designed to demonstrate the biological denitrification process developed at ORNL. The pilot plant will be installed at the Portsmouth Gaseous Diffusion Plant (operated by the Goodyear Atomic Corporation) and will treat the plant's solvent extraction raffinate waste stream.

Results obtained with engineering-scale equipment are the basis for the pilot-plant design. These results using 5-cm-ID and 10-cm-ID bioreactors indicated that the bioreactor diameter can be scaled up if the liquid superficial velocity is held constant. Results using single and dual 10-cm-ID by 6-m-tall bioreactors compared satisfactorily with the empirical fit of the data obtained earlier with the single 5-cm-ID bioreactor and test results using actual Portsmouth waste in the 10-cm-ID bioreactor (Figure 9) were as predicted by the empirical curve. Therefore, we have a basis for designing and predicting the performance of the mobile pilot plant for a field test specific to the Portsmouth Gaseous Diffusion Plant streams.

The mobile pilot-plant will contain two reactors 20·cm ID, a scale-up factor of 4. This is acceptable considering the good comparison of the previous factor of 4 scale-up data from 5 to 10 cm ID. The superficial

(116)

Data from

Portsmouth feed

(Present in semi-annual Report)

Fig. 9.

velocity will be held constant at 0.84 cm/sec, corresponding to a flow rate of about 16 liters/min. The length of each reactor was chosen to be 7 m because sufficient head room is available at Portsmouth. Using Figure 10 to estimate the operating conditions, we concluded that a feed of 4000 g/m^3 NO$_3^-$ would produce a near-zero NO$_3^-$ effluent concentration for this total reactor length.

The bioreactors will be fabricated of stainless steel tubing, divided into three flanged sections about 2.4 m long. The tapered solid-liquid disengaging zone is 3 m long and has a maximum diameter of 36 cm ID.

The main frame sections, which are designed for each of assembly, will be fabricated from 10-cm square structural tubing.

The schematic flowsheet for the pilot plant with Portsmouth raffinate waste is given in Figure 11. The flow path starts with the delivery of 185 liters of raffinate daily to the 700-liter neutralization tank. The raffinate is diluted with water to make 300 to 400 liters and is then neutralized with NaOH to pH 8.0. The predilution and pH adjustment facilitate settling of the precipitated metals (Fe, Al). Bacteria may be added at this point to remove heavy-metal ions. The precipitate will be removed by settling or centrifugation. The solid will be drummed for storage. The pH of the clear feed will be adjusted to 7.0 for biological denitrification.

A piping and equipment flowsheet for the biological denitrification is given in Figure 12. Alcohol for a carbon source, phosphate, and other micronutrients needed for bacterial growth will be added to the feed at the bottom of the bioreactor to decrease the chance of precipitation, which is sometimes experienced with concentrated waste streams. Water or recycle effluent will also be added to the feed concentrate at the bottom of the bioreactor to dilute the NO$_3$ concentration to 4000 g/cm^3. This dilute nitrate
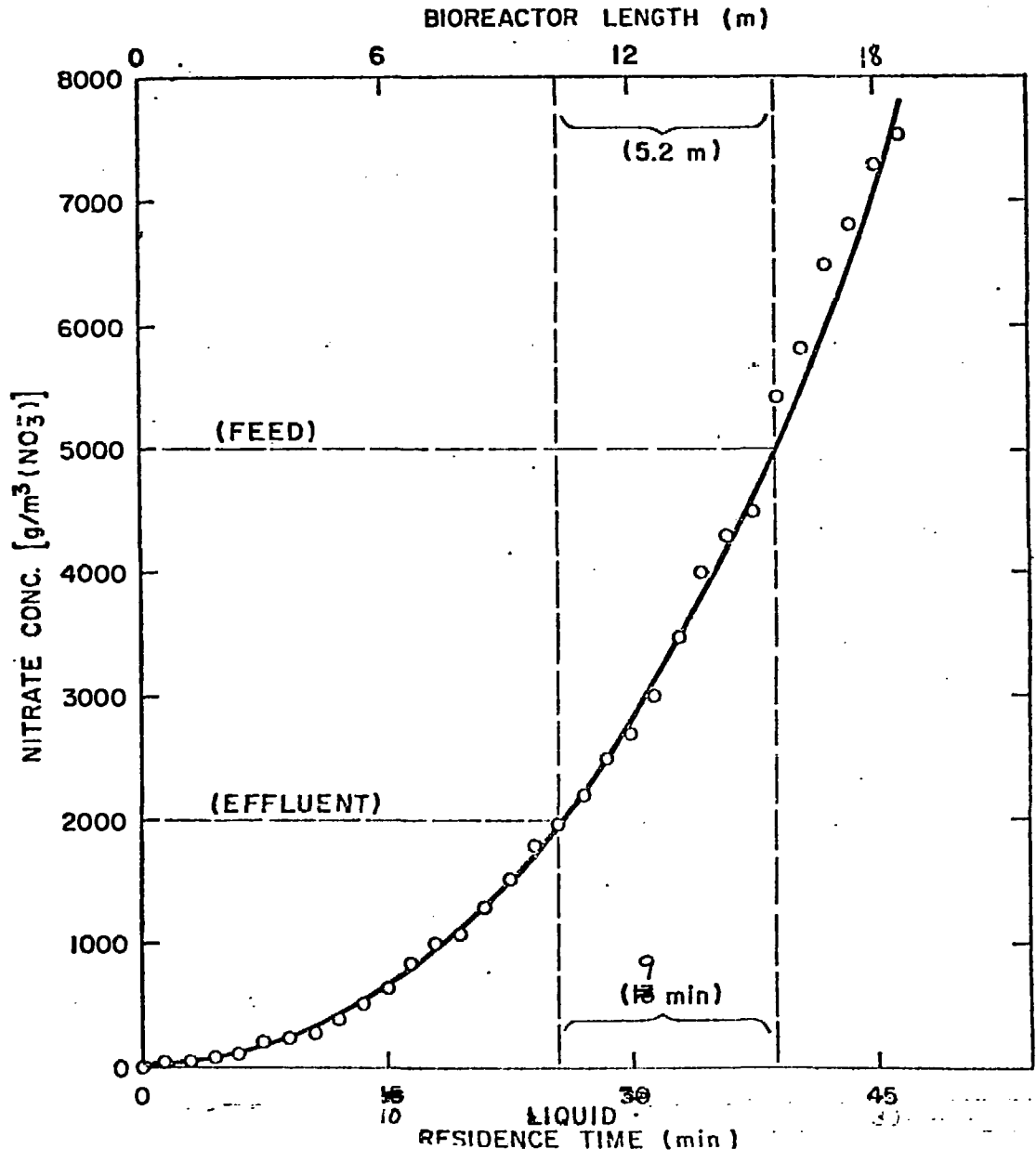
Note: This fig. is being corrected

Fig. 10. Nitrate concentration vs bioreactor length for a number of tests compressed into one curve.
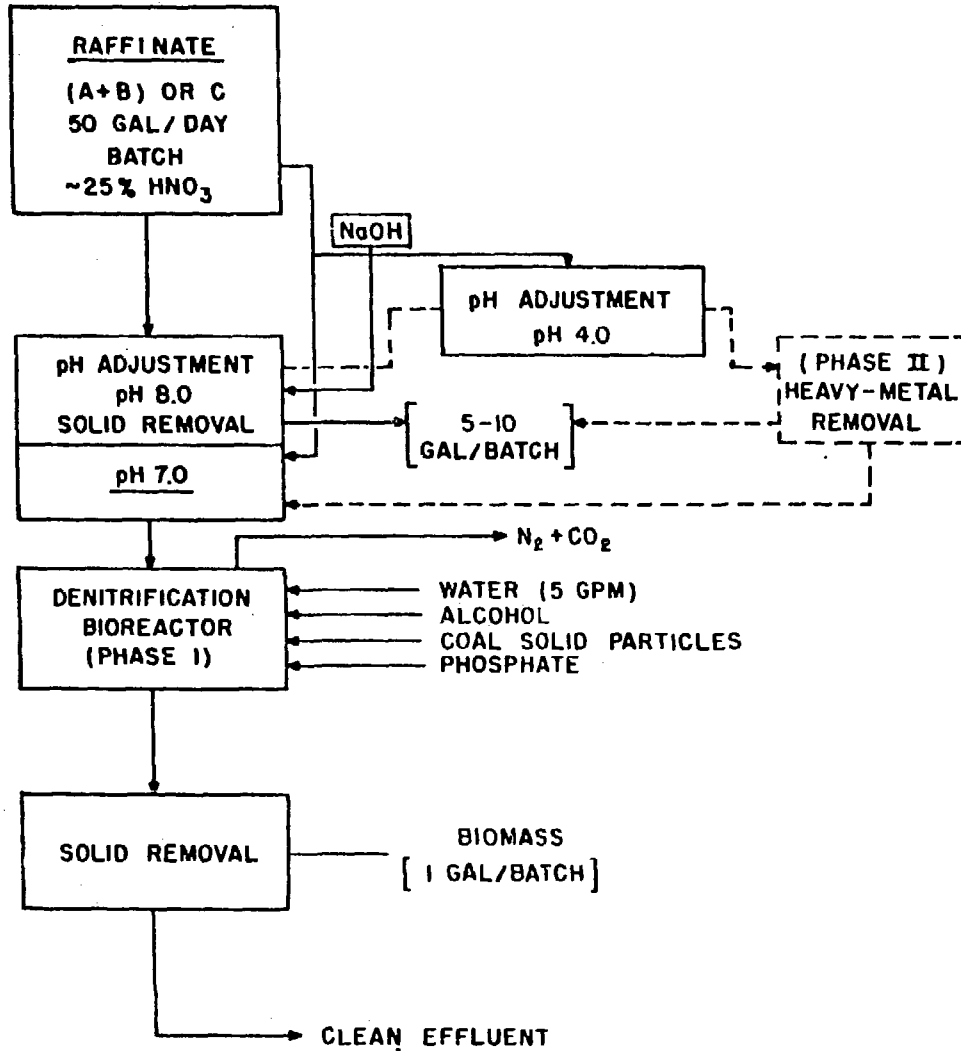
ORNL DWG 78-9746

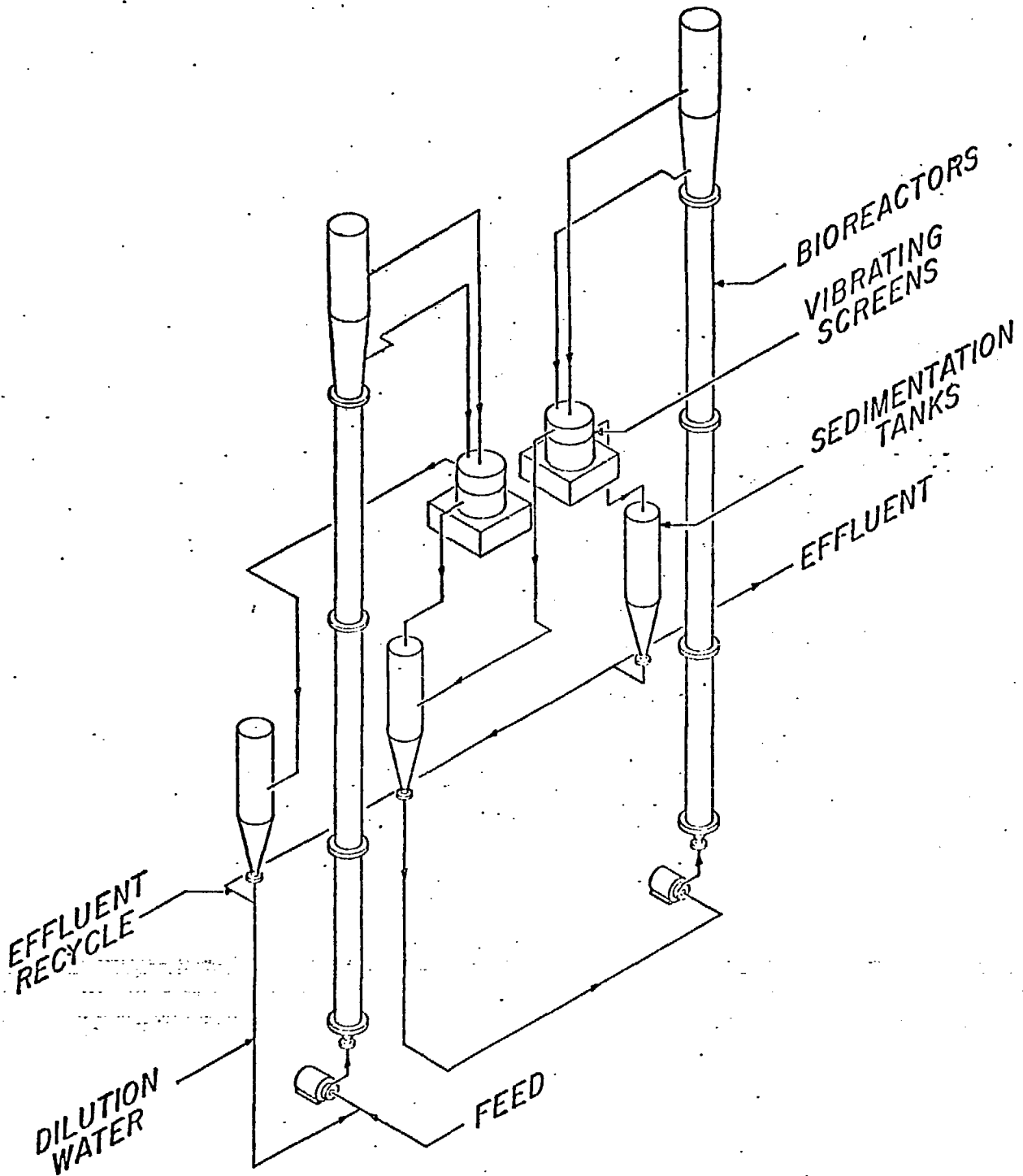BIODENITRIFICATION FLOWSHEET

Fig. 22. Schematic flowsheet.

Fig. 12. Piping and equipment flowsheet.

waste is continuously fed to the two denitrification bioreactors in series. The fluidized coal particles are continuously withdrawn from the bioreactors and fed to the vibrating screens where excess biomass is removed. The cleaned particles are recycled to the bottom of the bioreactors. Effluent from the second bioreactor is discharged with near-zero NO_3^- concentration.

CONCLUSIONS

A strong case has been made for the use of biological processes for removing nitrates and heavy metals from nuclear fuel cycle effluents. The estimated costs for these methods are as low as, or lower than, those for alternate processes. In addition, the resulting disposal products--nitrogen gas, CO_2, and heavy metals incorporated into microorganisms--are much more ecologically desirable than the end products of other waste treatment methods.

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