

CONF-800447--1

BIOLOGICAL DENITRIFICATION OF HIGH-NITRATES WASTES
GENERATED IN THE NUCLEAR INDUSTRY

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INTRODUCTION

Biological denitrification appears to be one of the most effective methods to remove nitrates from wastewater streams (Christenson and Harremoes, 1975). However, most of the research and development work has been centered on removal of nitrates from sewage or agricultural drainage waters (Cooper, 1977 and McCarty, 1969); nitrate nitrogen concentration usually less than 50 g/m^3 . Work was initiated at Oak Ridge National Laboratory (ORNL) in 1974 to test the use of biological nitrification in the removal of high concentrations of nitrate (in excess of $1.0 \text{ kg NO}_3\text{-N/m}^3$) from uranium purification waste streams (Auerbach, et al., 1974; Clark, et al., 1975; and Francis and Callahan, 1975). Since then, a full-scale treatment facility, a stirred reactor, has been installed at the Y-12 plant; and a pilot-plant, using a fluidized bed, has been proposed at Portsmouth Gaseous Diffusion Plant (Hancher, et al., 1978).

The objective of this manuscript is to present some applied microbiological research relating to possible constraints in biologically denitrifying certain waste streams in the nuclear industry and comparing the effectiveness of denitrification of these waste streams in three bench scale reactors, (1) a continuous flow-stirred reactor (CFSR), (2) a stirred bed reactor (SBR), and (3) a fluidized bed reactor (FBR).

NITRATE WASTES IN THE NUCLEAR INDUSTRY

Nitrate wastes are generated throughout the nuclear fuel cycle; uranium milling, uranium hexafluoride production, uranium enrichment, and fuel fabrication and reprocessing (Pechin, et al., 1975). Not to be excluded are all the high- and intermediate-level radioactive wastes which have been dissolved or suspended in caustic nitrate solutions and stored in large, underground carbon steel tanks (Ondrejcin, 1974). In the past, discharge of nitrate via dilution

into the environment was tolerated; however, present state and federal regulations do not allow such discharges, thus methods of disposal need to be assessed and implemented. Currently, many nuclear facilities are simply temporarily storing their waste in shallow, impermeable, lined lagoons, while evaluating various nitrate recycle and disposal systems (calcination, catalytic decomposition, fertilizer production, ion exchange, and biological removal processes). Many of these waste streams not only contain high nitrate concentrations (in excess of 20% HNO_3), but also concentrations of Al, F, Cu, Ni, and other metals that may inhibit biological denitrification.

FACTORS INFLUENCING RATES OF DENITRIFICATION OF VARIOUS WASTE STREAMS IN THE NUCLEAR INDUSTRY

Radiation Effects: Low and high level radioactive wastes contain from 0.2 to 6.4 M concentrations of nitrate (Ondrejcin, 1974). Removal of nitrates from such wastes will enhance the wastes vitrification properties, reduce waste solids, and decrease nitrate stress-corrosion cracking of waste supernates stored in steel tanks. To test the influence of acute radiation on the efficiency of denitrifying microorganisms, 10 ml of an actively denitrifying culture were exposed to the following radiation doses; 10^3 , 10^4 , 10^5 , and 10^6 Rads. After the accumulated dose from a ^{60}Co source (approximately 3×10^5 Rads per hour), the 10 ml suspension of denitrifying microorganisms were mixed with 25 ml of a nitrate solution composed of 0.016 M HN_4NO_3 , 0.027 M NH_4OAc , 1 mM MgSO_4 , 0.32 mM KH_2PO_4 , and 2 g of Fe/m^3 as sodium ferric diethylenetriamine pentaacetate (Fe-DTPA). The solutions were purged with N_2 and nitrate concentrations monitored over time. Radiation doses greater than 10^5 Rads were required to decrease denitrification rates. Thus, if a mean life-time of a denitrifying bacterium is taken to be 24 hours (Table 1), a dose rate of ca. 0.3 Rad/s would be required to deliver 10^5 Rads. These data indicate γ -radiation per se (levels up to 0.3 Rad/s) will not inhibit denitrification

rates; however, exposure to chronic radiation doses at these high levels will likely produce chemical effects such as the production of H_2O_2 and hydrolysis products that may inhibit denitrification more than any direct effect of radiation.

Table 1
Influence of Acute Radiation on Biological Denitrification Rates

Radiation Rads	Time (Days) ¹							Denitrification Rates ²	
	0	1	3	4	6	7	10	λ days ⁻¹	R ²
	----- g/m ³ of NO ₃ -N -----								
0	166	141 ^a	---	22 ^a	---	15 ^a	---	0.38	0.92
10 ³	166	142 ^a	---	28 ^a	---	20 ^a	---	0.33	0.92
10 ⁴	166	155 ^a	---	18 ^a	---	10 ^a	---	0.44	0.93
10 ⁵	166	146 ^a	---	53 ^b	---	12 ^a	---	0.38	0.98
10 ⁶	166	---	161	---	100	---	20	0.21	0.48
Control ³	230			232	235				

¹Numbers in the same column with similar superscripts are not significantly different at the 5% probability level. All treatments except the 10⁶ Rad dose were replicated three times.

² $\hat{y} = ae^{-\lambda t}$, where \hat{y} is estimated NO₃-N in g/m³, a is initial NO₃-N concentration, λ is first order rate constant in days⁻¹ and t is time in days. R² = Coefficient of determination of least squares fit.

³Nitrate solutions similar to other treatments except no denitrifying microorganisms were added.

Nitrate Concentration: To operate a biological denitrification facility most effectively, one must be aware of the maximum and minimum nitrate substrate concentrations required for the engineering design. In a single stage continuous flow-stirred reactor, substrate nitrate concentrations are not likely to be inhibitory as their concentration are usually low enough for discharge to the environment. However, in multiple stage reactors, and particularly in the

case of columnar denitrification (stationary or fluidized beds), it is advantageous to use the maximum nitrate concentrations in the influent stream without inhibiting the denitrification rate. Nitrate wastes in the nuclear industry are highly concentrated (often greater than $50 \text{ kg NO}_3\text{-N/m}^3$), and require dilution before direct exposure to denitrifying microorganisms. Thus, the nitrate substrate levels that are toxic or inhibitory to biological denitrification should be avoided. Earlier work using NH_4NO_3 solutions in continuous flow-stirred reactors indicated that nitrate concentrations greater than $1.7 \text{ kg NO}_3\text{-N/m}^3$ inhibited denitrification rates (Francis and Mankin, 1977).

To test the influence of nitrate on denitrification using $\text{Ca}(\text{NO}_3)_2$, six treatments in triplicate were made of varying nitrate concentrations. Carbon was provided as calcium acetate and remained constant for each treatment (2.08 kg C/m^3). The nitrate and nitrite concentration were monitored the next six days (Table 2) to determine the respective denitrification rates.

Table 2
Influence of Nitrate Concentration on Denitrification Rates

Initial Nitrate Concentration	Total Nitrate Removed ¹	Denitrification Rate ²	
----- $\text{kg NO}_3\text{-N/m}^3$ -----	-----	$\frac{\text{mg NO}_3\text{-N}}{\text{m}^3 \text{ s}}$	R^2
5.03	0.40	1.16	0.481
2.28	0.86	1.62	0.971
1.90	0.97	2.60	0.999
1.15	0.87	2.55	0.999
0.95	0.84	2.60	0.992

¹After six days

²Rate for first two days, R^2 = coefficient at determination of least squares fit from 18 observations.

To evaluate the effect of initial nitrate concentrations, rates were determined

based on the first two days of the experiment. All coefficients of determination (R^2) were greater than 0.970 at initial nitrate concentrations $< 2.28 \text{ kg NO}_3\text{-N/m}^3$. These rates were used with nitrate substrate concentrations after one day, viz, the average nitrate concentration over the first two days to determine any inhibition using a Hanes-Woolf plot (Segel, 1975). These data indicated that inhibition in denitrification occurred between substrate nitrate levels of 1.7 and 2.1 $\text{kg NO}_3\text{-N/m}^3$ and were very similar to those observed (1.7 $\text{kg NO}_3\text{-N/m}^3$) in continuous flow-stirred reactors using NH_4NO_3 as a nitrate source and methanol as a carbon source (Francis and Mankin, 1977).

Influence of Acetate as a Carbon Source: Excessive levels of the carbon source, as well as the nitrate, might inhibit denitrification. Acetate has been used as a carbon source in biological denitrification (Clark, et al., 1975).

Although generally more expensive than ethanol or methanol, it is nonflammable and thus, storage does not represent a safety hazard as do ethanol or methanol; particularly at processing facilities that handle highly enriched uranium. A similar experiment, as described above, was designed to evaluate the influence of acetate levels on denitrification rates. Acetate levels ranged from 0.80 to 13.0 kg C/m^3 while initial nitrate levels were kept below 1.0 $\text{kg NO}_3\text{-N/m}^3$.

The rate of denitrification (Table 3) appears to be more sensitive to increasing levels of acetate than nitrate. For example, nitrate removal at 6.65 kg C/m^3 of acetate was less than one-half the removal rate at 0.84 kg C/m^3 . Using these rates and the initial acetate concentrations in a Hanes-Woolf plot, showed that acetate concentrations greater than 6.5 kg C/m^3 were highly inhibitory. Even acetate concentrations in excess 2.0-2.5 kg C/m^3 appeared to inhibit denitrification. On the other hand, methanol at concentrations of 3.75 kg C/m^3 did not inhibit denitrification (Francis and Mankin, 1977). Work presented in a later section of this manuscript showed that no inhibitory effects of methanol were observed at methanol concentrations of 7.5 kg C/m^3 . These data indicate

that if high nitrate substrate concentrations are desired in biological denitrification, care should be taken with regard to quantity and type of carbon source selected.

Table 3
Influence of Acetate on Denitrification Rates

Initial Acetate Concentration kg C/m ³	Total Nitrate Removed ¹ kg NO ₃ -N/m ³	Denitrification Rate ²	
		mg NO ₃ -N m ³ s	R ²
13.1	0.03	0.17	0.321
6.65	0.22	1.30	0.947
5.36	0.30	1.77	0.992
3.4	0.31	1.82	0.998
2.78	0.33	1.92	0.997
2.13	0.47	2.70	0.974
0.84	0.53	3.08	0.978

¹After two days

²Rate for first two days, R² = coefficient of determination of least squares fit from 18 observations.

Complementary Cation-Ca and NH₄: The two dominant complementary cations in most nitrate waste streams are calcium and ammonium. Ammonium nitrate wastes are generated predominately in uranium recovery operations which use the ammonium diuranate process. Calcium nitrate wastes are often associated with the milling of uranium and other operations where limestone or hydrated lime have been used to neutralize excess nitric acid wastes.

The denitrification rates of nitrate supplied as these two forms [Ca(NO₃)₂ and NH₄NO₃] were compared under identical conditions using an initial concentration of 1.2 kg NO₃-N/m³ (Table 4). Carbon was supplied as the acetate salt of either calcium or ammonium (2.32 kg C/m³), respectively.

Table 4

Biological Denitrification Rates of Ca and NH₄ Nitrate Solutions

Nitrate Salt	Total Nitrate Removed ¹	pH ¹	Denitrification Rate ²	
	kg NO ₃ -N/m ³		$\frac{\text{mg NO}_3\text{-N}}{\text{m}^3 \text{ s}}$	R ²
Ca(NO ₃) ₂	0.51	6.7	2.85	0.972
NH ₄ NO ₃	0.35	8.7	1.95	0.990

¹After two days

²Rate for first two days, R² = coefficient of determination of least squares fit from 18 observations.

The denitrification rate of nitrate supplied in the form of Ca(NO₃)₂ was approximately 1.5 times faster than that supplied as NH₄NO₃. Three factors might be responsible for the slower rate with NH₄NO₃, viz, (1) excessive ammonium concentrations, (2) higher ambient pH levels, and (3) higher levels of soluble carbonate and bicarbonate than in solutions made of calcium nitrate. With Ca(NO₃)₂ solutions, the calcium carbonate solubility product was exceeded on the biological conversion of acetate to CO₂, which in turn kept the pH lower than with NH₄NO₃ solutions. On the other hand, in the NH₄NO₃ solutions, bicarbonate and carbonate accumulate, each of which could possibly be an inhibitor. Data to be presented later in this manuscript and that published earlier (Francis and Mankin, 1977) indicate little differences in rates between Ca and NH₄ nitrate solutions in continuous flow-stirred reactors or tapered fluidized beds. The above data (Table 4) shows that under identical initial conditions, calcium nitrate solutions are denitrified faster than ammonium nitrate solutions.

Ammonium Concentrations: Ammonium nitrate wastes are generated by UO₂ fuel fabrication plants that use the ammonium diuranate process for recycling UO₂.

Maximum levels of ammonium that are non-toxic to denitrification are needed to determine the maximum permissible influent concentrations of NH_4NO_3 , and the quantity of effluent that may be recycled for dilution water. To test the influence of ammonium, two ammonia salts NH_4Cl and $(\text{NH}_4)_2\text{CO}_3$ were used at four levels of $\text{NH}_4\text{-N}$ (1.0, 2.0, 3.5, and 5.0 kg/m^3) in nitrate solutions (1.37 $\text{kg NO}_3\text{-N/m}^3$ as $\text{Ca}(\text{NO}_3)_2$).

Increasing NH_4Cl concentrations decreased denitrification rates (highly linear, $R^2 = 0.934$). The inhibition, however, was interpreted to be due to chloride rather than ammonium. Using $(\text{NH}_4)_2\text{CO}_3$, on the other hand, showed no significant differences in denitrification rates up to 3.5 $\text{kg NH}_4\text{-N/m}^3$. At 5.0 $\text{kg NH}_4\text{-N/m}^3$, the denitrification rate was 64% of the observed average rate at 1.0, 2.0, and 3.5 $\text{kg NH}_4\text{-N/m}^3$. Thus, influent concentrations in excess of 3.5 $\text{kg NH}_4\text{-N/m}^3$ would not be recommended until further testing is carried out.

Nickel Concentrations: "Poisoning" of a biological reaction by trace levels of certain heavy metals is a major concern regarding the feasibility of using biological denitrification as a waste treatment process. In the nuclear industry, nitric acid is used to clean or "decontaminate" equipment. Much of this equipment is made of various grades of steel which contains high concentrations of nickel. Because nickel is known to be toxic to many biological systems, an experiment was conducted to evaluate the toxicity of nickel on biological denitrification.

The data below (Table 5) indicates that initially very low concentrations of Ni significantly inhibit denitrification rates. For example, 0.5 g Ni/m^3 reduced denitrification nearly 50% the first three days. Note that the added Ni did not become immediately sorbed to either the microbial biomass or suspended material, nor did it immediately precipitate as the carbonate. After 13 days, over 50% still remained in solution. The most interesting point is that after

8 days, the levels of Ni (as high as 3.9 g/m³ soluble Ni) were not inhibitory, indicating a Ni tolerant microbial population had been selected.

Table 5
Effect of Nickel on Denitrification¹

Treatment Ni g/m ³	Time (Days)							
	0	2	3	8	9	10	13	
	-----			NO ₃ -N g/m ³	-----			
0	1310	860	280	< 2	1160	1020	650	< 2
0.5	1310 (0.51)	930	400 (0.49)	< 2 (0.48)	1160	1000 (0.47)	650 (0.44)	< 2 (0.32)
1.0	1310 (0.97)	1030	480 (0.97)	< 2 (0.96)	1160	980 (0.91)	610 (0.93)	< 2 (0.73)
5.0	1310 (5.00)	1310	1110 (4.90)	< 2 (3.70)	1160	930 (3.90)	590 (3.60)	< 2 (2.30)

¹Numbers in parentheses are soluble nickel concentrations (g/m³) after centrifuging 20,000 RPM for 20 min. (34,880_{av} RCF); Ni-63 used as a tracer to determine nickel concentrations. Nitrate concentrations are the averages of three treatment replications. On day 8, additional Ca(NO₃)₂ and Ca(OAc)₂ were added.

Sodium Tolerance - Culture Selection: Caustic soda rather than limestone or hydrated lime has been used to neutralize nitric acid wastes (Ondrejcin, 1974). Earlier work has indicated that denitrification rates with sodium salts were appreciably lower than those observed with calcium or ammonium nitrates. Of greater significance was the large concentrations of nitrite in the effluents (Francis and Malone, 1977).

Probably the most important factor in the biological denitrification of high nitrate wastes is establishing a microbial culture that is tolerant to solutions of high ionic strength. Logical sources of such cultures are the oceans, estuaries, and other saline environments. A screening test was carried out to

observe if the source of the denitrifying culture was important in denitrifying at high sodium concentrations (0.5 - 1.0 M Na) and pH's (> 9.0). Denitrifiers from three sources were compared over 90 days in batch stirred reactors: (1) a culture from the denitrifying reactor at the Y-12 plant, (2) a culture seeded from the surface horizon of a highly productive agricultural soil from Wisconsin, and (3) a culture seeded from an estuarine marsh sediment from the coast of California.

All cultures sustained denitrification at sodium concentrations as high as 0.8 to 1.2 M and at these sodium concentrations there appeared to be no difference in rates (0.6 - 2.0 $mg\ NO_3-N/m^3/s$). The most significant observation made in these tests was the very high denitrification rates using the denitrifying cultures isolated from the estuarine sediment at the sodium concentrations between 0.5 and 0.7 M (concentrations very similar to sea water) and at pH's > 9.1. These rates (on the order of 7 $mg\ NO_3-N/m^3/s$) were twice those observed in the cultures isolated from the soil, and six times those observed using cultures from the Y-12 denitrification plant. Cultures seeded from this estuarine sediment were used in the following bench scale tests.

BENCH SCALE TESTS

Three bench scale reactors, (1) a continuous flow-stirred reactor (CFSR), (2) a stirred bed reactor (SBR), and (3) a fluidized bed reactor (FBR) were used to evaluate the effectiveness of denitrifying synthetic high-nitrate wastes made from NH_4 , Ca, and Na nitrates (Fig. 1). The CFSR (8.3 L) consisted of a glass carboy in which a denitrifying culture was suspended with a magnetic stirring bar. Influent was delivered to the bottom and the effluent exited the top (flow rate $0.13 \pm 0.02\ cm^3/s$). The SBR was made from a glass pipe (68.5 x 10.2 cm ID) that contained 3.7 L of anthracite coal (sieved to the 250-590 μm range). The bed was very slowly stirred (2 RPM) with a stainless steel stirrer

(1.3 cm wide paddles angled 0.52 radians every 3.8 cm along a 0.27 cm diameter shaft). The fluidized bed reactor tapered from a 2.54 to a 5.08 cm diameter opening at the bottom and top respectively contained 0.54 L of the same sieved anthracite coal as the SBR. The bed was fluidized using a recirculating peristaltic pump (1.3 cm³/s). Influent flow ranged from 0.15 to 0.20 cm³/s. The efficiencies of the reactors were expressed in mgNO₃-N/m³/s based on bed volumes for SBR and FBR and total volume for CFSR.

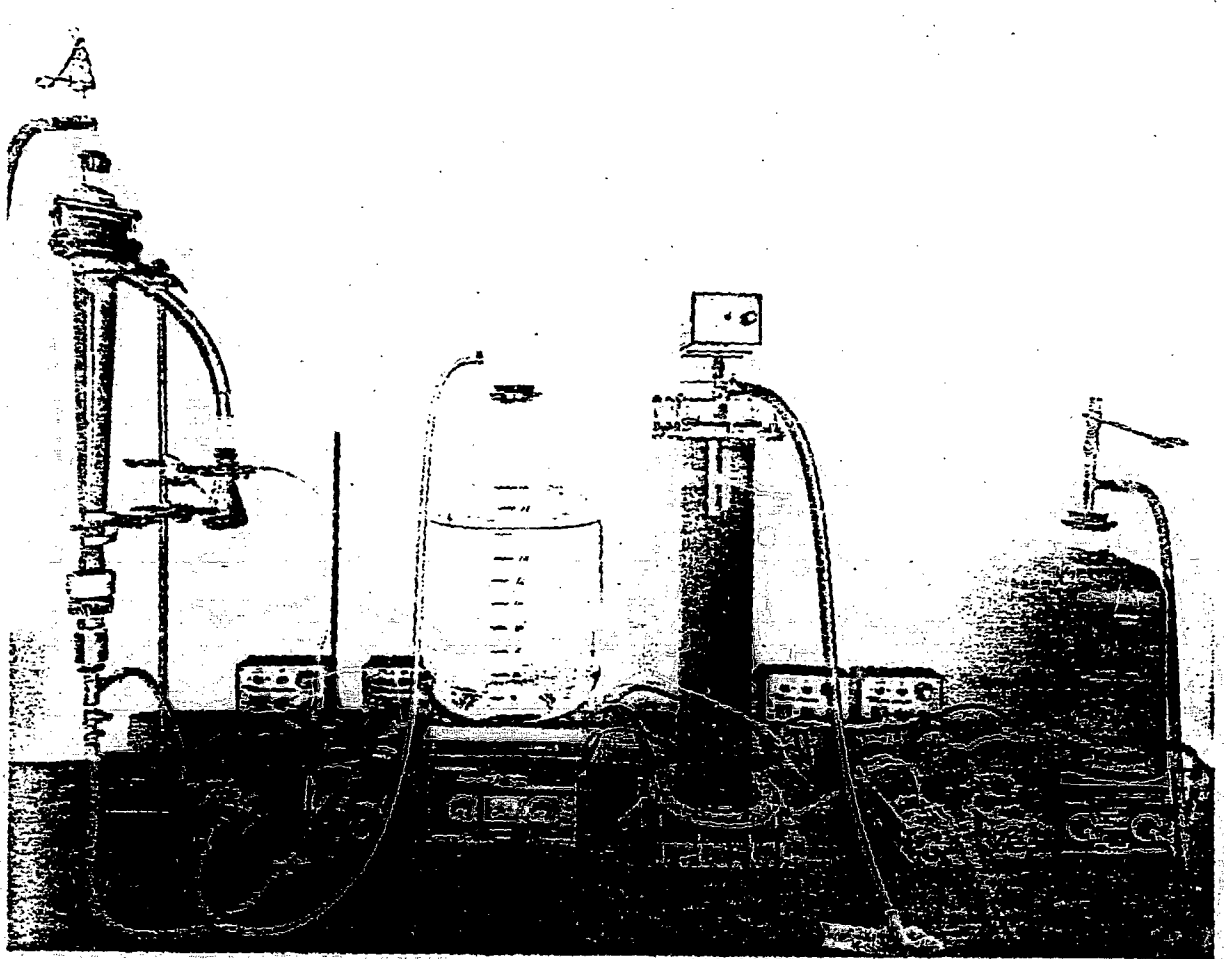


Figure 1.

Three bench-scale denitrification reactors used to evaluate microbiological parameters influencing the denitrification of high-nitrate wastes.

Influence of Methanol: Methanol in concentrations ranging from 1.5 to 30 kg C/m³ was added to influent nitrate solutions (approximately 1 g NO₃-N/m³) of

the FBR (Table 6). The reactor was operated for one day at each methanol concentration.

Table 6
Influence of Methanol on Denitrification¹

Time Day	Methanol kg C/m ³	Denitrification Rate
		mg NO ₃ -N m ³ s
1	1.51	74.0
2	7.55	82.1
3	15.1	81.0
4	22.7	51.8
5	30.7	41.5

¹In fluidized-bed tapered column with 0.54 L of anthracite coal (250-590 μ m diameter particles).

Inhibition in denitrification was not observed until the concentration of approximately 23 kg C/m³ of methanol was used. Using acetate in the earlier tests showed that inhibition occurred as low as 6 kg C/m³. These data imply that methanol may be more suitable as a carbon source in high-nitrate denitrification than acetate. For example, using a ratio of 1.4 g C/g NO₃-N, methanol would be a likely candidate as a carbon source to denitrify high-nitrate wastes in the range of 5.0 to 10.0 kg NO₃-N/m³.

Nitrate Concentration: The influence of increasing nitrate concentrations on rates of denitrification using NH₄, Ca, and Na nitrate solutions were determined in the FBR using a microbial culture selected from an estuarine sediment. The experimental plan was to establish base-line denitrification rates at concentrations < 1 kg NO₃-N/m³, and then increase influent nitrate concentrations every 24 hours by increments of 1 kg NO₃-N/m³. Previous work has shown inhibition to occur in the vicinity of 2 kg NO₃-N/m³. Influent flow rates were

maintained to keep the hydraulic residence time < 5 hours.

Using NH_4NO_3 solutions, the rate of denitrification increased on increasing nitrate concentration (Fig. 2). The response, however, is not as absolute as

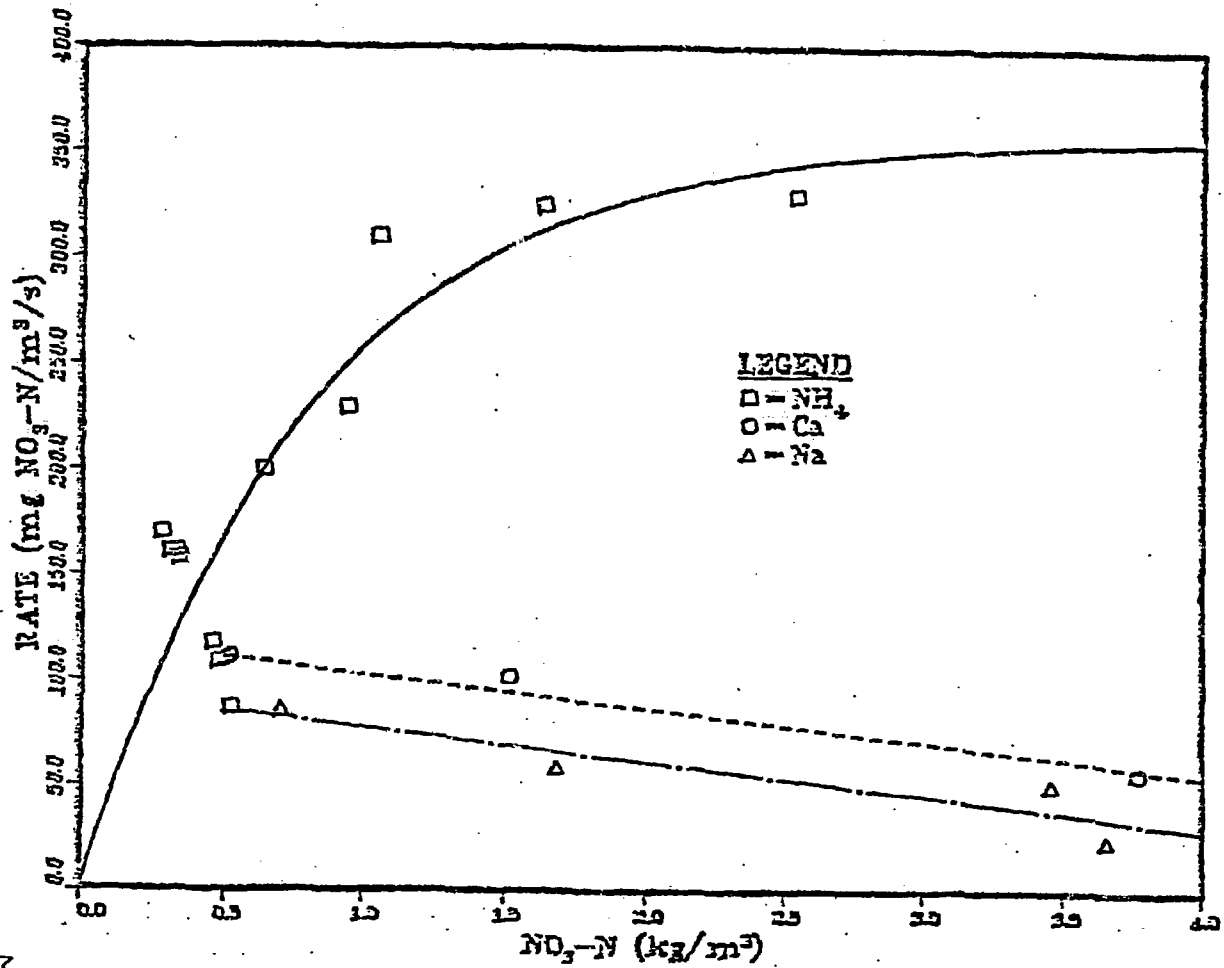


Figure 2.

Influence of increasing levels of three nitrate solutions (NH_4 , Ca , and Na) on the denitrification rate in a fluidized bed reactor.

it may appear, as the base-line data before increasing the influent nitrate concentration showed significant increases as a function of time. For example, the rate increased from 90 to 200 $\text{mg NO}_3\text{-N}/\text{m}^3/\text{s}$ over a 16 day interval at substrate concentrations of approximately 0.5 $\text{kg NO}_3\text{-N}/\text{m}^3$. Increasing influent nitrate concentration accelerated the increasing denitrification rate. The

significant observation is that maximum denitrification was observed at a nitrate substrate concentration in excess of $2.5 \text{ kg NO}_3\text{-N/m}^3$.

Increasing nitrate concentration did not increase the denitrification rate when $\text{Ca}(\text{NO}_3)_2$ or NaNO_3 solutions were used. In fact, the opposite was observed (Fig. 2). The response was probably not due to the nitrate concentration per se, but very likely due to the complementary cation, Ca or Na. The mechanisms, however, are probably different. In the case of Ca, the decrease in the rate of denitrification could be due to a phosphorus deficiency. Earlier work had shown denitrification is highly dependent on available phosphorus. Using $\text{Ca}(\text{NO}_3)_2$ at a $\text{NO}_3\text{-N}$ concentration of 0.8 kg/m^3 (Ca conc. $3.5 \times 10^{-2} \text{ M}$), the total soluble phosphorus is on the order of 0.4 g P/m^3 ; however, on increasing to $4.0 \text{ kg NO}_3\text{-N/m}^3$ the calculated soluble P is $< 0.1 \text{ g/m}^3$ (using K_{sp} of CaHPO_4 equal to 10^{-7} and pH 6.5). Thus, even though 10 g P/m^3 were added to the influent solutions, the quantity of soluble P delivered to the FBR is limited by the solubility of CaHPO_4 . This is unlike the experiments above that were carried out in batch reactors where the phosphorus was in the reactor. As denitrification proceeds, the Ca concentrations are rapidly lowered by CO_3^- production to less than 10^{-2} M . For FBR influent concentrations of $\text{Ca}(\text{NO}_3)_2 < 1 \text{ kg NO}_3\text{-N/m}^3$, rates obtained for $\text{Ca}(\text{NO}_3)_2$ were very similar to those using NH_4NO_3 (av. max. $218 \pm 38 \text{ mg NO}_3\text{-N/m}^3/\text{s}$). However, the fluid properties of the bed soon deteriorated because of CaCO_3 accumulation in the bed.

The decreasing rates observed with increasing concentrations of NaNO_3 solutions appeared to be due to the toxic influence of Na. Even at concentration $< 1 \text{ kg NO}_3\text{-N/m}^3$, switching from NH_4 to Na nitrate solution always resulted in lower denitrification rates. On the other hand, switching between NH_4 and Ca nitrate showed no difference in rates of denitrification. Maximum denitrification rate observed using NaNO_3 solutions was $< 100 \text{ mg NO}_3\text{-N/m}^3/\text{s}$. Portsmouth's nitric acid waste neutralized to 7.5 with NaOH was half as effective as neutralizing

to the same pH with $\text{Ca}(\text{OH})_2$ (70 versus 153 mg $\text{NO}_3\text{-N}/\text{m}^3/\text{s}$).

Comparison Among Reactors: Maximum denitrification rates (using NH_4NO_3) were 330, 23, and 5.3 g $\text{NO}_3\text{-N}/\text{m}^3/\text{s}$ for FBR, SBR, and CFSR, respectively. Based solely on the denitrification rate, the FBR is by far the superior reactor design for denitrification of high-nitrate wastes. Other factors, such as character of the waste and environmental discharge constraints, however, may dictate the choice of reactor design. For example, unless the bed is continuously regenerated, Ca nitrate solutions will result in an accumulation of CaCO_3 that will affect the fluidization properties of a FBR. As an alternative, acidic nitrate wastes can be neutralized with caustic soda followed by a FBR. The denitrification rates may be significantly lower, however, even at NaNO_3 concentrations between 5 and 7 kg $\text{NO}_3\text{-N}/\text{m}^3$ the rates (25-50 mg $\text{NO}_3\text{-N}/\text{m}^3/\text{s}$) were equivalent to NH_4NO_3 and $\text{Ca}(\text{NO}_3)_2$ rates in SBR (Clark, et al., 1975). Use of Na neutralized nitric acid wastes at these concentrations might be restricted because of the high pH, nitrite [earlier work (Francis and Malone, 1977) using different microbial cultures showed nitrite conc. as high as 300 g $\text{NO}_2\text{-N}/\text{m}^3$, although concentrations greater than 10 g $\text{NO}_2\text{-N}/\text{m}^3$ were not detected in this work], alkalinity, and dissolved salts in the effluent will exceed environmental discharge levels in certain states and countries. From this standpoint, the reactor design used at the Oak Ridge Y-12 Plant has certain advantages. In this design, nitric acid raffinate (> 50 kg $\text{NO}_3\text{-N}/\text{m}^3$) containing high concentrations of Al (> 15 kg/ m^3) are fed continuously to a CaCO_3 SBR in which the sludge [composed of 11% solids consisting of CaCO_3 and $\text{Al}(\text{OH})_3$] is withdrawn batchwise and disposed in a landfill. The design also has the advantage in that the water requirements are considerably less than that required for a FBR.

SUMMARY AND CONCLUSIONS

1. Acute doses of radiation as high as 10^5 Rads did not significantly reduce

the rate of denitrification.

2. Nitrate solutions made from $\text{Ca}(\text{NO}_3)_2$ showed inhibition in denitrification between 1.7 and 2.1 kg $\text{NO}_3\text{-N/m}^3$.
3. Calcium acetate as a carbon source was highly inhibitory at carbon concentrations greater than 6.5 kg/m³.
4. High calcium solutions likely limit denitrification because of limited phosphorus availability.
5. Ammonium at concentrations of 5.0 kg $\text{NH}_4\text{-N/m}^3$ inhibited denitrification.
6. Nickel concentrations as low as 0.5 g/m³ inhibited denitrification, however, after 8 days a microbial population tolerant to as much as 3 g/m³ was selected.
7. Methanol concentrations as high as 15 kg C/m³ were not inhibitory to denitrification.
8. In FBR, nitrate solutions > 2.5 kg $\text{NO}_3\text{-N/m}^3$ made from KH_4NO_3 were denitrified much more effectively than those from Ca or Na nitrate. At concentrations < 1 kg $\text{NO}_3\text{-N/m}^3$, no significant differences were noted in rates of denitrification between Ca and NH_4 nitrate solutions; however, rates with Na nitrate solutions were consistently slower.
9. The best reactor design for high-nitrate wastes at a specific facility will be determined by composition of waste stream (elements such as Al, Ca, etc., as well as nitrate), effluent discharge constraints, available process water, as well as reactor efficiency.
10. Denitrification efficiency in a FBR was found to be 10-15 times higher than in a SBR, and approximately 50 times higher than in a CFSR.

The above conclusions apply to any industry that produces high-nitrate wastewater since the biological and engineering constraints are the same. Engineering designs will not vary substantially between treatment of high-nitrate wastewater in the nuclear industry and other industries. In summary, the choice of base used for neutralization, and the quantity of solids generated

and easy of removal will dictate engineering design. Denitrification rates in fluidized beds are significantly higher than that in stirred-bed reactors, and is the preferred engineering design for many waste streams that do not require solids removal prior to denitrification.

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Research sponsored by the Office of Nuclear Energy Products/Waste, U. S. Department of Energy, under contract W-7405-eng-26 with Union Carbide Corporation.

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The author wishes to acknowledge the assistance of C. W. Hancher, Oak Ridge National Laboratory and J. M. Napier, Oak Ridge Y-12 Plant in preparing this manuscript.